6. INTERACTIONS OF AGENTS WITH ELASTOMERS AND LUBRICANTS

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6.1 Introduction

Elastomers and greases used in fire suppression systems serve to prevent container leakage and subsequent suppression system malfunction due to insufficient fire suppressant agent or container pressure. Excessive swelling or mechanical deterioration, particularly of the elastomeric seals, can lead to such leakage. The goal of the work undertaken in this part of the project was to obtain data on the compatibility of elastomeric seals and greases with candidate fire suppression agents. In the process a methodology was developed to obtain data that characterizes the swelling of elastomers and resistance of elastomers to mechanical degradation in the presence of the candidate elastomers.

In the first phase of the project short term exposure experiments were conducted to characterize the compatibilities of 11 agents with 6 commonly used elastomers and 3 lubricants (McKenna et al., 1994). Two types of measurement techniques were developed and used:

(i) swelling measurements due to sorption of the agent into the elastomers (or lubricants) at four different temperatures from 35 °C to 150 °C, and

(ii) durability measurements, which produced data on residual mechanical (rheological) properties of the elastomers (and lubricants) after exposure to the agents at 150 °C and 5.86 MPa.

Based on the results of the swelling tests a rating system was proposed to characterize the compatibility of elastomers (and lubricants) with the different agents. In swelling measurements good compatibility (i.e., an elastomer or lubricant is acceptable for use with the fire suppressant) was defined as the value of the Flory-Huggins polymer-solvent interaction parameter (χ) determined at 35 °C being larger than 1.2. Bad compatibility ($\chi < 0.9$) corresponds to excessive swelling. For values of $0.9 < \chi < 1.2$, the agent was considered to have fair compatibility with the elastomer or lubricant and represents a marginally acceptable system.

In the measurements of the residual mechanical properties, compatibility ratings were to have been based on the results of compression set and tensile test data of the elastomers. The important conclusion to be drawn from the durability testing was that the 150 °C temperature was too high for reasonable evaluation of changes in the mechanical properties of candidate elastomers and greases and that the degradation resistance after long term exposure of the elastomeric materials could not be estimated from the results. Therefore, in the cases of the four agents selected for further testing (HFC-227ea, HFC-125, FC-218, and CF$_3$I (not considered in the first phase of the project)) measurements were performed at 50, 75 and 100 °C. The temperature 75 °C was chosen to conduct the long-term mechanical property measurements. Information from the sponsors indicated that all-metal storage containers are used for exposures above 70 °C. Further testing of the greases was not considered necessary.

This report summarizes the work performed in FY 1994-95 and is organized as follows: Section 6.2 describes the results of the swelling measurements for seven sets of crosslinked and uncrosslinked elastomers in the 3 selected fire suppressant agents. (Note that in the first phase of the project only six elastomers were investigated. The seventh elastomer, ethylene-propylene-diene (EPDM) terpolymer was suggested by NIST for completeness of the study because it is a widely-used, environmentally-inert elastomer.) The results are compared with those obtained for halon 1301 which serves as a baseline to compare the properties of the fluorocarbon alternatives. In Section 6.3 the results of the durability measurements are shown. A Kohlrausch-Williams-Watt (KWW) type stretched exponential function (Williams and Watt, 1970) is used to describe the compression set data. This function is used to predict the changes in the mechanical properties after long exposure times. In Section 6.4 the results obtained for iodotrifluoromethane (CF$_3$I) are presented. This chemical was not investigated in the first phase of the project. Later it was recommended for inclusion by the sponsor of the program because it was found to be as effective as halon 1301 in suppressing non-premixed

flames. Since testing in this agent was accompanied by several specific problems, the results of these investigations are discussed separately. In Section 6.5 the results of the thermodynamic (swelling) investigations in combination with the durability measurements are summarized.

6.2 Swelling Measurements

6.2.1 Theoretical Background.

A polymer exposed to a thermodynamically compatible diluent absorbs solvent molecules. The driving force of the mixing process is mainly entropic. The Flory-Huggins lattice theory of polymer solutions (Flory, 1942; Huggins, 1943, Flory 1953) describes the free energy of mixing and allows the characterization of the affinity of the polymer (elastomer or lubricant) to the solvent (fire suppressant agent) by a single polymer-solvent interaction parameter χ.

In a swelling measurement the concentration of the polymer at equilibrium is measured as a function of solvent activity a_1 (Boyer, 1945; Gee $et\ al.$, 1965; Brotzman and Eichinger 1982 and 1983; Horkay and Zrinyi, 1982; McKenna $et\ al.$, 1989; Horkay $et\ al.$, 1989; McKenna $et\ al.$, 1990; McKenna and Crissmann 1993). According to the Flory-Huggins theory:

$$\ln a_1 = \ln(p/p^o) = \ln(1 - v_2) + (1-1/P)v_2 + \chi v_2^2 \tag{1}$$

where p is the equilibrium vapor pressure of the diluent, p^o is its saturation vapor pressure, v_2 is the volume fraction of the polymer, P is the degree of polymerization and χ is the Flory-Huggins polymer-solvent interaction parameter. In general χ depends on the polymer volume fraction (Flory, 1970), $i.e.$, $\chi=\chi_0 + \chi_1 v_2 + ..$, where χ_0 and χ_1 are constants.

From Equation (1) it follows that the measurement of the equilibrium polymer volume fraction as a function of the vapor pressure of the diluent allows the determination of the χ parameter, i.e., the estimation of the solubility of elastomers in the fire suppressant agents. Small χ values ($\chi < 0.5$) correspond to solubility across the whole concentration range. In this case uncrosslinked polymers are completely dissolved and crosslinked polymers exhibit large swelling which can lead to seal failure in elastomeric o-ring based joints. High χ values are characteristic of polymer/solvent systems with limited miscibility.

Although the Flory-Huggins theory is formulated in terms of volume fractions (v_1 and v_2), the theory can also be expressed in terms of weight fractions (w_1 and w_2). This substitution does not change the functional form of Equation (1), i.e.,

$$\ln(p/p^o) = \ln(1 - w_2) + w_2 + \chi_0 w_2^2 + \chi_1 w_2^3, \tag{2}$$

where $\chi = \chi_0 + \chi_1 w_2$ has been substituted, and the term $(1 - 1 / P)$ has become unity since P is large for polymeric materials and infinite in crosslinked networks. In this case the χ values differ from those calculated from the equilibrium volume fractions (v_1 and v_2). Throughout the present report weight fractions are used instead of volume fractions because they are directly measured quantities.

Table 1.   Elastomers used in swelling experiments

Elastomer	Vendor	Designation
Silicone	Colonial Rubber	Si
55% Butadiene-45% Acrylonitrile	Goodyear	N206
Fluorosilicone	Colonial Rubber	FSi
Viton E-60 Fluorocarbon	Du Pont	FKM
Neoprene	Colonial Rubber	CR
85% Butadiene-15% Acrylonitrile	Goodyear	N926
Ethylene-Propylene-Diene	Exxon	EPDM

Table 2.   Lubricants used in swelling experiments

Lubricant	Vendor	Designation
Krytox 240AC Fluorinated Grease	Du Pont	240AC
Braycote 600 Perfluoropolyether Grease, Low Volatility	Castrol	600
Braycote 807 Aircraft Grease MIL-G-27617, Type IV	Castrol	807

6.2.2 Experimental Materials and Methods. The elastomers and lubricants used in this study are shown in Tables 1 and 2, respectively.[1] Both crosslinked and uncrosslinked elastomers were investigated. The 85 % butadiene-15 % acrylonitrile crosslinked copolymer was prepared according to a method described earlier (McKenna et al., 1994). The silicone, fluorosilicone, neoprene, and ethylene-propylene-diene polymers were supplied crosslinked and uncrosslinked by the vendor. The fluorocarbon polymers were cured at NIST for one hour at 150 °C and post-cured at 240 °C for 24 hours.

The swelling measurements were performed in an apparatus (Figure 1) described earlier (McKenna et al., 1994). The pressure vessels were made of type 304 stainless steel and designed for a maximum working pressure of 5.86 MPa with two view ports 180° apart for viewing and backlighting purposes.

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[1]Certain trade names and company products are mentioned in the text or identified in an illustration in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

Table 3.   Saturation data for agents

Trade name	Formula	Chemical name	p^o @ 35°C - (MPa)	p^o @ 70 °C (MPa)	p^o @ 105°C (MPa)	T_c (°C)	p_c (MPa)
HFC-227ea	C_3HF_7	heptafluoropropane	0.615	1.49	--	101.7	2.91
HFC-125	CHF_2CF_3	pentafluoroethane	1.78	--	--	66.3	3.62
FC-218	C_3F_8	octafluoropropane	1.15	2.41	--	71.9	2.68
halon 1301	CF_3Br	bromotrifluoromethane	2.04	--	--	67	3.96

T_c: critical temperature
p_c: critical pressure
p^o: saturation vapor pressure

Samples weighing 25-50 mg were placed on quartz pans suspended from quartz springs (see Figure 1). The sensitivity of the springs was either 1 mg/mm or 1.25 mg/mm. The vessels were placed in a cylindrical Pyrex jar and completely immersed in silicone bath oil. Two rectangular holes were made so that the view ports were visible. The bath was heated using an immersion heater and stirred to maintain temperature uniformity. A pressure charging and recovery system was used for admission of the agent into the vessel and for recovery of it after each measurement.

The mass uptake by elastomers and lubricants was calculated from the displacement of the quartz spring measured by a cathetometer. Measurements were taken at 35, 70, 105 and 150 °C as a function of the vapor pressure. For each test temperature the agent vapor pressure was varied between the saturation pressure at the test temperature and that at the next (lower) temperature. In this way undesired saturation during cooling, which could ruin the samples, was avoided. Above the critical temperature T_c of the agent the upper limit of the pressure range was the maximum working pressure of the apparatus (5.86 MPa). Saturation pressures for each temperature were determined for agents HFC-125, FC-218, and halon 1301 using thermodynamic properties software (Gallagher *et al.*, 1991), and for agent HFC-227ea from vendor supplied data (Robin, 1992) and are shown in Table 3.

After measurements were performed for all temperatures considered, the vessel was evacuated and the spring displacements were checked for reversibility. Where appropriate, corrections for buoyancy effects were made (McKenna et al, 1994).

6.2.3 Results and Discussion of the Swelling Measurements.

In Figures 2-5, typical plots of solvent weight fraction w_1 *vs.* vapor pressure p are shown for different elastomer/agent systems. The fluid uptake of the elastomers considerably increases with the vapor pressure and decreases with increasing temperature (Figure 5). In Figures 6-8, the experimental data obtained at 35 °C are shown according to the Flory-Huggins representation. The curves are the least squares fits of Equation (2) to the data points. In Tables 4 and 5 are listed the values of the Flory-Huggins interaction parameters ($\chi = \chi_0 + \chi_1$) determined for the elastomers in the three selected agents and in halon 1301. (Similar data for the three agents and the six elastomers were given in the 1994 report (McKenna et al. 1994). In order to check the reproducibility of the swelling tests we repeated these measurements. The previous values of χ are given in parentheses in Tables 4 and 5. The results indicate that the repeatability of the χ data is, generally, better than 5 %.) In Table 6 the χ values are shown for the three lubricants. χ measures the solubilities (compatibilities) of the subcritical agents in various polymers. It is apparent from the data that the values of the interaction parameters for the crosslinked
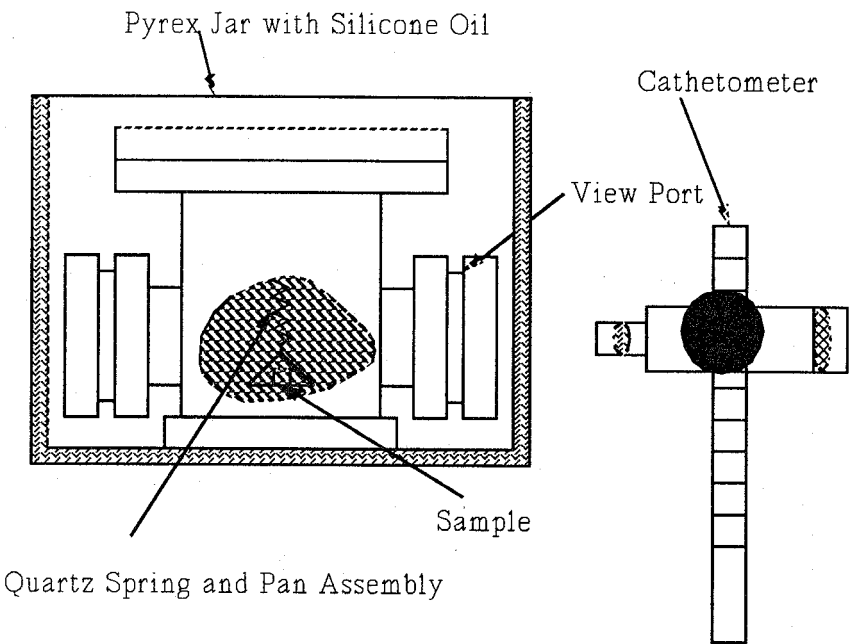
Pyrex Jar with Silicone Oil

Cathetometer

View Port

Sample

Quartz Spring and Pan Assembly

Figure 1.   Schematic drawing of the experimental apparatus for isopiestic swelling measurements.

Table 4.   Flory-Huggins interaction parameters χ for subcritical temperatures studied for different agent/elastomer systems

Agent (T °C)	u[c]CR	x[d]CR	u N926	x N926	u EPDM	x EPDM
227ea (35)	1.25 (1.25[b])	1.34 (1.33[a])	0.78 (0.80)	0.84 (0.84)	1.31	1.34
227ea (70)	1.29 (1.31)	1.44 (1.38)	0.85 (0.85)	0.88 (0.87)	1.35	1.37
125 (35)	1.99 (4.10[b])	2.03 (1.99)	1.22 (1.23)	1.26 (1.28)	1.98	2.02
218 (35)	1.64 (1.63)	1.70 (1.68)	1.62 (1.56[b])	1.71 (1.71)	1.53	1.58
218 (70)	1.74 (1.75)	1.77 (1.77)	1.67 (1.69)	1.74 (1.74)	1.62	1.70
halon 1301 (35)	1.98	2.08	1.25	1.12	1.06	1.12

[a]$12.5 < CV < 20\%$ and $0.64 < \chi < 1.5$ (35 °C)
[b]$CV > 20\%$ (35 °C)
[c]uncrosslinked polymer
[d]crosslinked polymer

polymers slightly exceed those of the corresponding uncrosslinked systems, i.e., the crosslinked polymer exhibits lower affinity to the solvent than its uncrosslinked counterpart. (Strictly speaking Equation (2) can only be applied for uncrosslinked polymers. The appropriate expression for a crosslinked polymer contains an additional term arising from the elasticity of the network (James and Guth, 1943; Flory and Rehner, 1943; Flory and Erman, 1982). For lightly crosslinked networks at high polymer concentration ($w_2 > 0.7$), however, this contribution is small in comparison to the mixing term.)

The rating system for characterizing the compatibility of the agents with the sealing materials was defined on the basis of the χ parameters determined at 35 °C. This temperature was chosen for several reasons. First, as shown in Figure 5, swelling is largest at 35 °C and gradually decreases with increasing temperature. Second, it is near the initial storage temperature of 25 °C. A good, bad, or fair rating is given for each agent/crosslinked elastomer system in Table 7.

The χ values shown in Tables 4-6 were calculated using a commercial software package. The curve fitter (SigmaPlot, Jandel, 1992) uses the Marquardt-Levenberg algorithm (Press *et al.*, 1986) to find the parameters which minimize the variance s^2 (ln p / p^0), i.e., the squared differences between the observed and predicted values of the dependent variable. The standard error or experimental standard deviation of the χ parameter, s (χ), and the coefficient of variation, $CV = 100s(\chi)/\chi$, were

Table 5.   Flory-Huggins interaction parameters χ for subcritical temperatures studied for different
            agent/elastomer systems

Agent (T °C)	u[c]Si	x[d] Si	u N206	x N206	u FSi	x FSi	u FKM	x FKM
227ea (35)	0.89	0.91	1.33	1.43	0.98	1.04	1.00	1.07
	(0.89)	(0.93[a])	(1.34[b])	(1.40[b])	(0.97)	(1.04[a])	(1.01)	(1.07[b])
227ea (70)	0.92	0.97	1.50	1.50	1.08	1.15	1.10	1.12
	(0.94)	(0.96)	(1.48)	(1.50)	(1.10)	(1.13)	(1.09)	(1.13)
125 (35)	1.26	1.32	1.69	1.75	1.34	1.36	1.17	1.24
	(1.29)	(1.30)	(1.69[b])	(1.72)	(1.33)	(1.35)	(1.18)	(1.21)
218 (35)	1.55	1.63	1.75	1.85	1.53	1.64	1.59	1.71
	(1.55)	(1.62)	(1.77[b])	(1.84)	(1.56[b])	(1.64)	(1.65)	(1.65)
218 (70)	1.60	1.71	1.90	1.99	1.66	1.75	1.68	1.63
	(1.64)	(1.69)	(2.04)	(1.99)	(1.67)	(1.74)	(1.66)	(1.67)
1301 (35)	0.92	0.97	2.15	2.16	1.04	1.11	1.69	1.71

[a] $12.5 < CV < 20\%$ and $0.64 < \chi < 1.5$ (35 °C)
[b] $CV > 20\%$ (35 °C)
[c] uncrosslinked polymer
[d] crosslinked polymer

also calculated for each χ value. Thus, the standard uncertainty of the parameter χ is $u(\chi) = s(\chi)$ and the percentage of relative standard uncertainty is shown in Tables 4 and 5 with superscripts.

Estimated values of χ for which $CV > 20\%$ are also shown with superscripts in Tables 4-6.

6.3 Mechanical Property Measurements

In order to characterize the long-term compatibility of the elastomers with the fire suppressant agents, mechanical property measurements (compression set and tensile testing) were performed after exposure times of 1, 2, 4, 8, 16, 32, 48 and 74 weeks. Exposure to the agents was carried out at 75 °C and 5.86 MPa, in pressure vessels similar to those used for the swelling measurements. Mechanical property measurements were also made after short term (1, 2 and 4 weeks) exposures at 50, 100, and 150 °C.

6.3.1 Compression Set. Measurements were carried out using standard test methods (ASTM, 1989 and 1990b). The o-rings used in this study were Parker No. 2-214 with a nominal cross section diameter (o-ring thickness) of 3.2 mm. The Parker compounds used are listed in Table 8. Specimens were prepared by cutting 52 mm sections from sample o-rings. The original thickness of each specimen was measured with a hand micrometer. Two specimens of each compound were placed in a

Table 6.   Flory-Huggins interaction parameters χ for the subcritical temperatures studied for each agent/lubricant system considered

Agent (T °C)	Krytox 240AC	Braycote 600	Braycote 807
227ea (35)	1.14[a]	0.93	0.93[b]
227ea (70)	1.23	0.97	1.02
125 (35)	1.18	1.37	1.35
218 (35)	1.83[b]	1.45	1.76
218 (70)	1.86	1.47	1.79
Halon (35)	1.36	1.50	1.57

[a] $12.5 < CV < 20\%$ and $0.64 < \chi < 1.5$ (35 °C)
[b] $CV > 20\%$ (35 °C)

compression set fixture. Each fixture consisted of two 18 cm diameter and 12.7 mm thick plates and seven spacers 2.65 ± 0.01 mm thick, 75 % of the measured mean value of the o-ring thicknesses. After removing from the fixture the specimens to be tested were kept at room temperature for a minimum of 30 minutes before measuring.   Measurements were taken at four marked locations equally distributed around the circumference in the axial direction, both on the unexposed samples and after each exposure time. The average value was used for subsequent calculations.

The compression set C is defined as

$$C = \frac{w_o - w_i}{w_o - w_n} \; x \; 100, \tag{3}$$

where w_o is the original average thickness of the o-ring, w_i is the o-ring thickness after exposure and w_n is the thickness of the fixture spacers.

In Table 9 are displayed the compression set results after each exposure time at 75 °C for all the elastomers in each fluorocarbon agent. As specified in Option 1 of the standards for compression set (ASTM, 1989 and 1990b), the value of compression set for each elastomer/agent system reported in Table 9 is the average of the compression set calculated from measurements of two samples. The sample standard deviation of the mean (sdm) of each pair of measurements was also calculated. The values of sdm obtained were 2 or less except for the fluorosilicone samples, for which the maximum value obtained was 4.4.

W₁
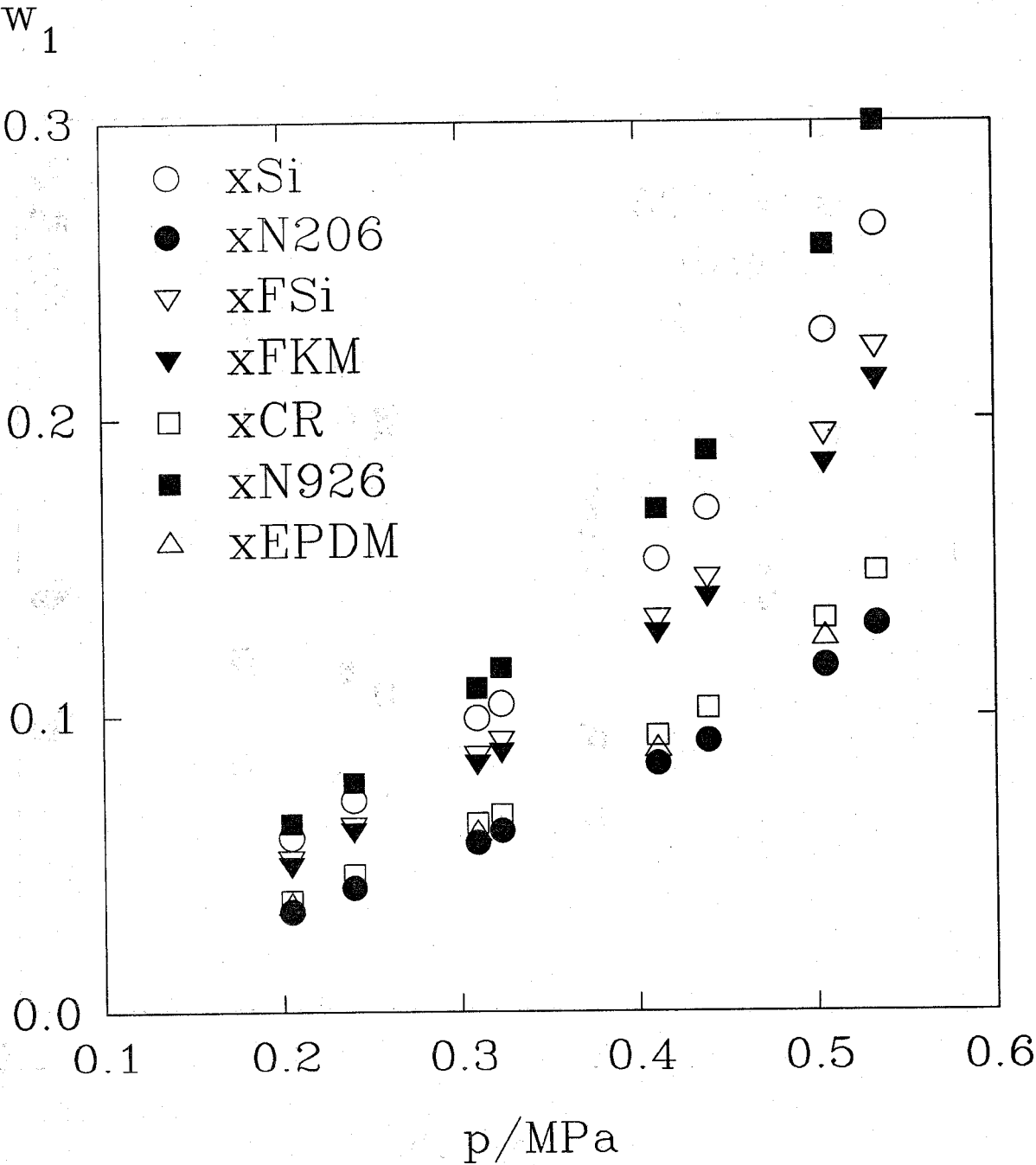
Figure 2.   Weight fraction w_1 of HFC-227ea as a function of pressure for various crosslinked
elastomers at 35 °C.
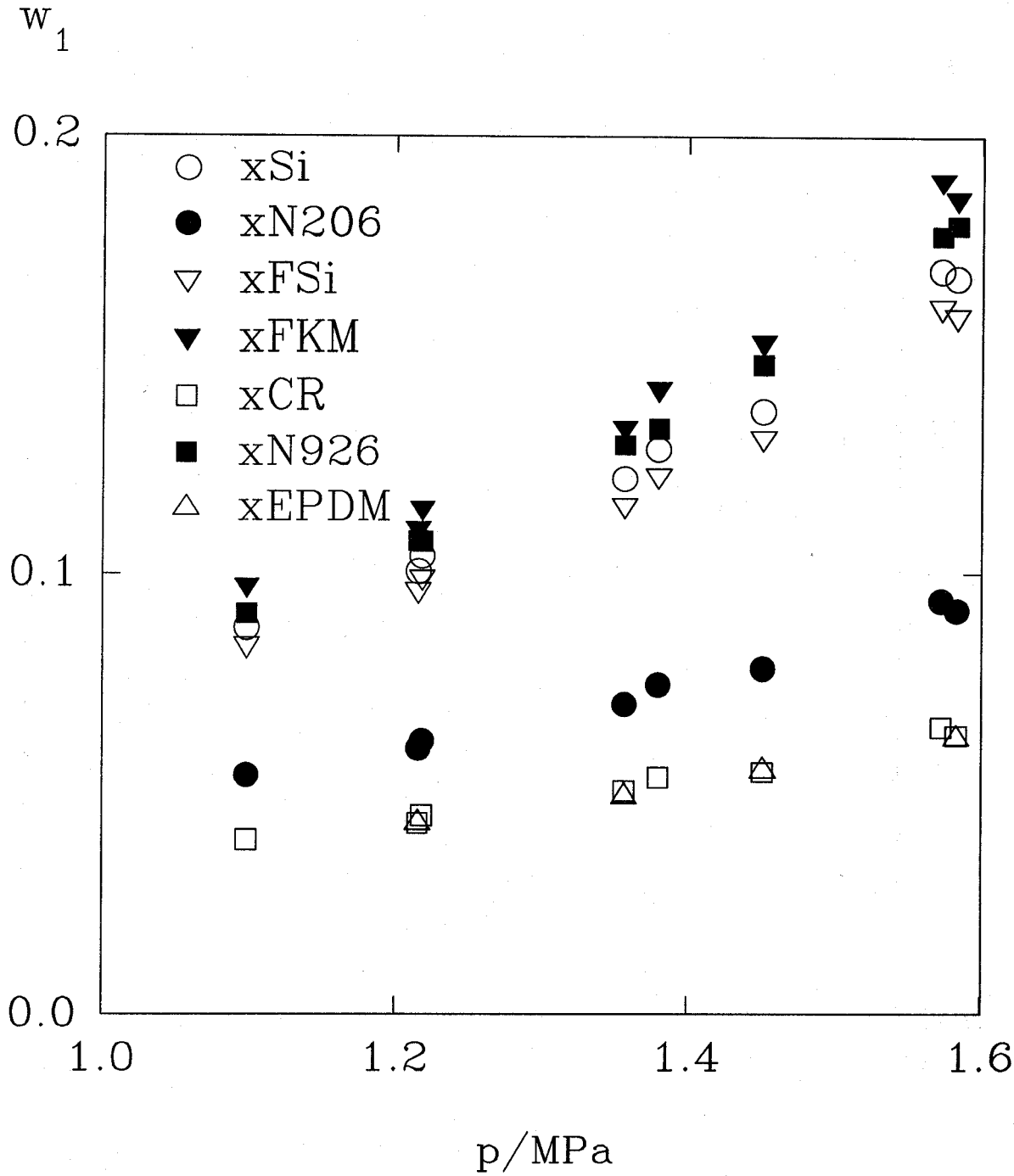
Figure 3.   Weight fraction w_1 of HFC-125 as a function of pressure for various crosslinked elastomers at 35 °C.

W_1
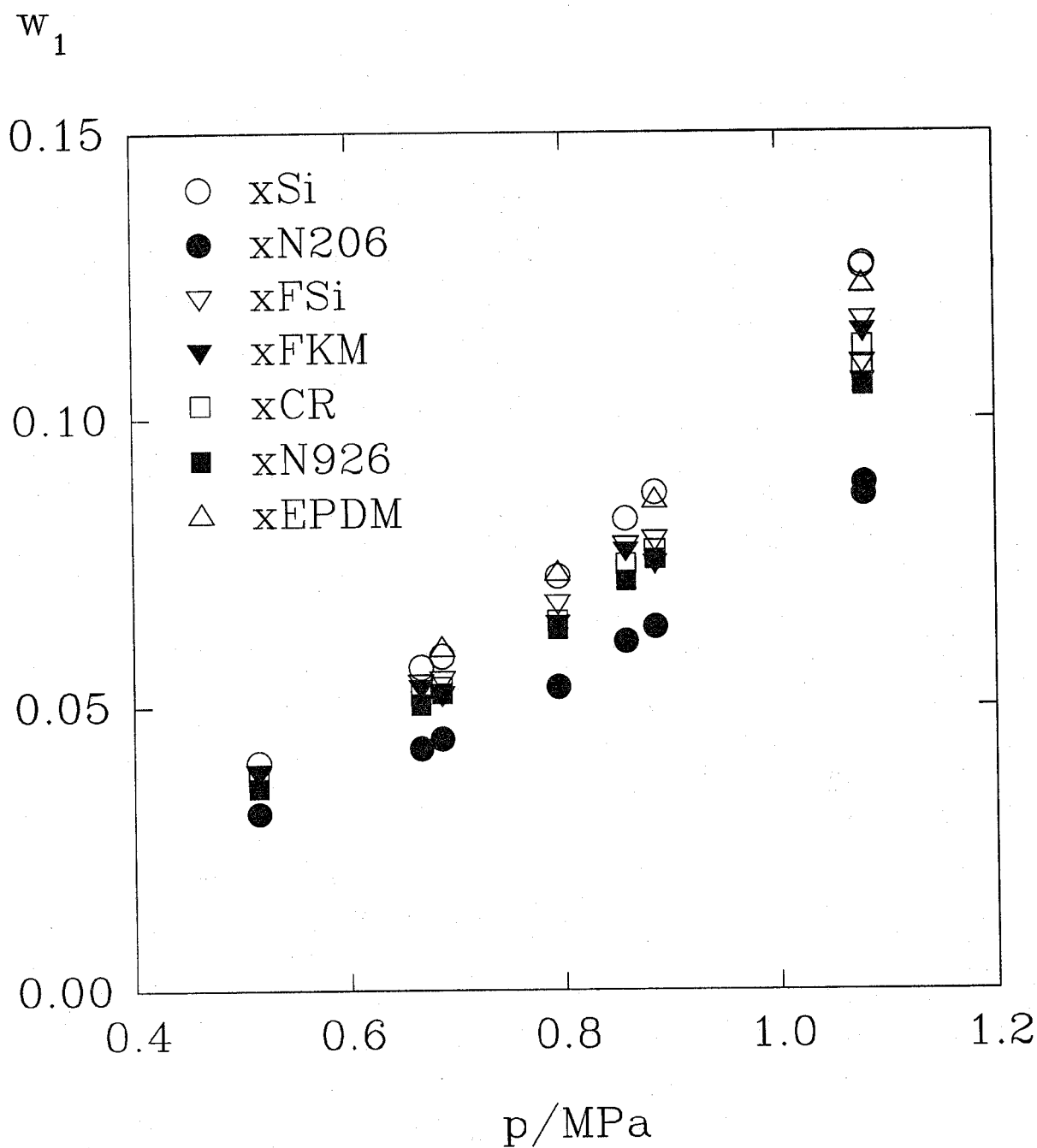
Figure 4.   Weight fraction w_1 of FC-218 as a function of pressure for various crosslinked elastomers at 35 °C.
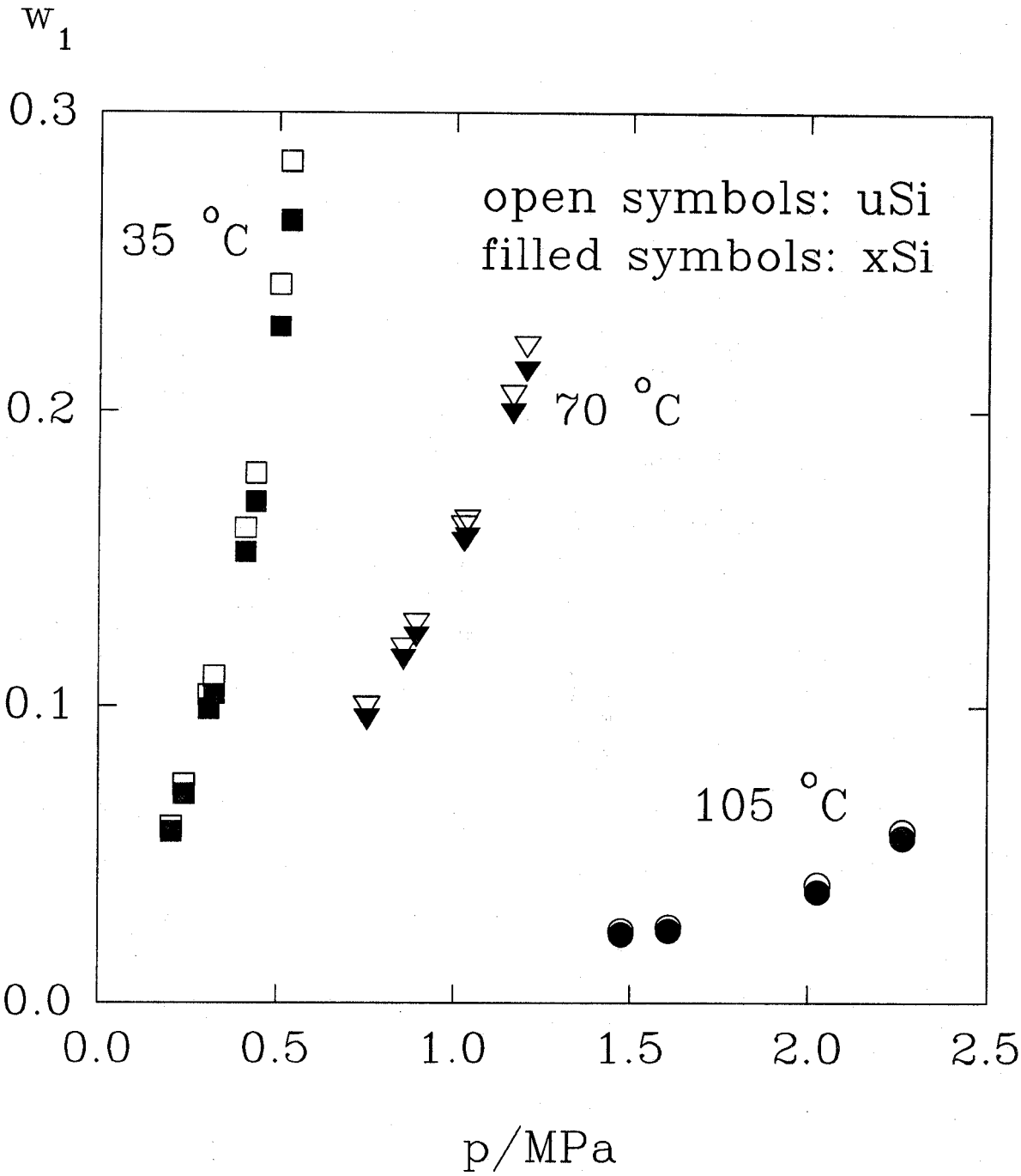
Figure 5. Weight fraction w_1 of HFC-227ea as a function of pressure in uncrosslinked and crosslinked silicone at various temperatures.
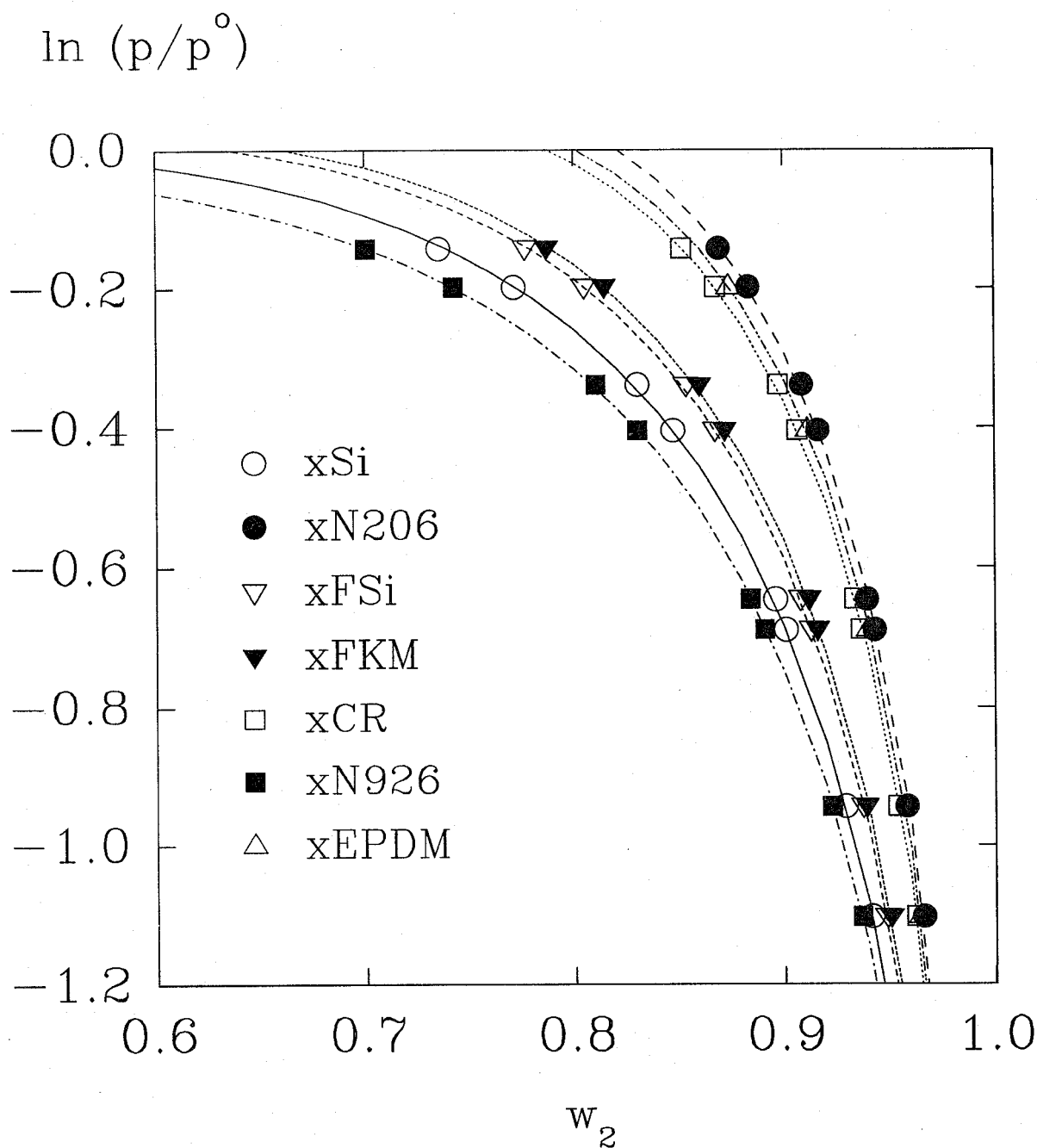
Figure 6.   Solvent activity in various crosslinked elastomers in HFC-227ea as a function of
polymer weight fraction w_2 at 35 °C. The curves show the least squares fits
according to Equation (2).

$\ln(p/p^{o})$
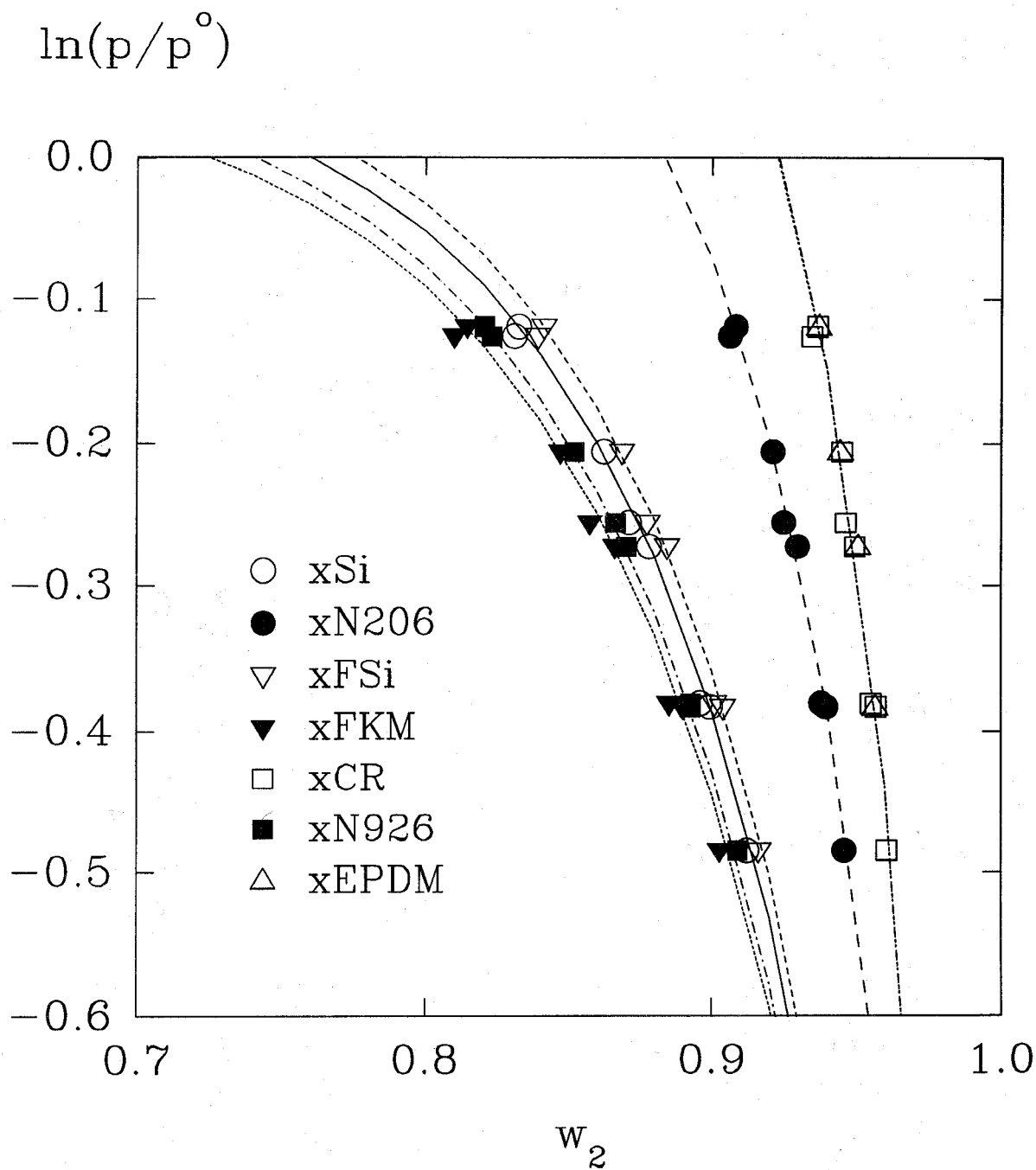
Figure 7.   Solvent activity in various crosslinked elastomers in HFC-125 as a function of polymer weight fraction w_2 at 35 °C. The curves show the least squares fits according to Equation (2).
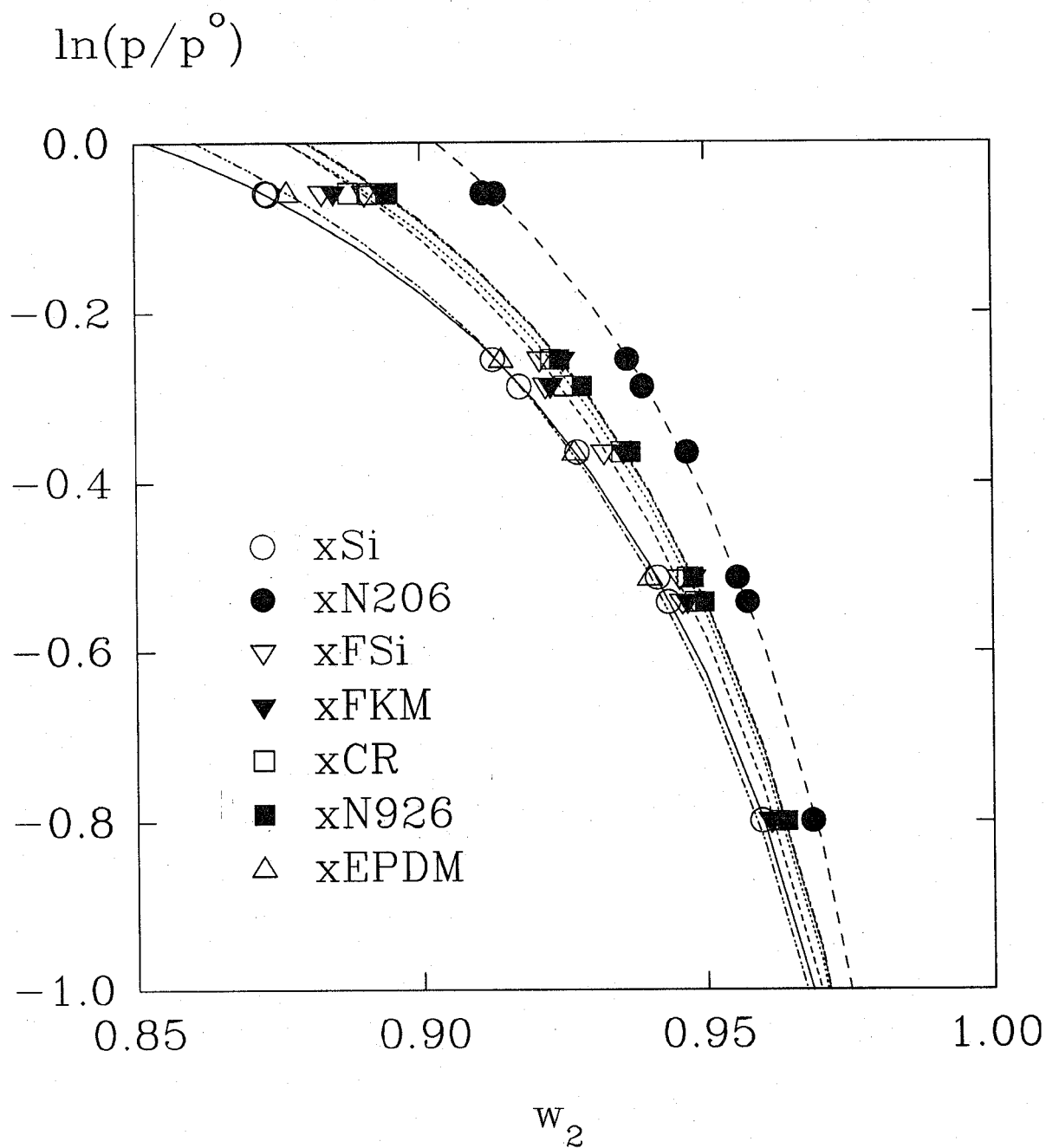
Figure 8.　　Solvent activity in various crosslinked elastomers in FC-218 as a function of polymer weight fraction w_2 at 35 °C. The curves show the least squares fits according to Equation (2).

Table 7. Compatibility of crosslinked elastomers based on swelling measurements in various fluorocarbon agents and halon 1301 at 35 °C.

Agent	Si	N206	FSi	FKM	CR	N926	EPDM
HFC-227ea	fair	good	fair	fair	good	bad	good
HFC-125	good	good	good	fair	good	good	good
FC-218	good	good	good	good	good	good	good
Halon 1301	fair	good	fair	good	good	good	fair

Table 8. Elastomers used in durability experiments

Elastomer	Vendor	Designation
Silicone	Parker	S604-70[a]
Nitrile (standard industrial)	Parker	N674-70
Fluorosilicone	Parker	L1120-70
Fluorocarbon	Parker	V1164-75
Neoprene	Parker	C1185-70
Nitrile (low temperature industrial)	Parker	N103-70
Ethylene-propylene-diene	Parker	E0540-80

[a]The number following the dash in the designation (compound number) represents the Shore hardness of the elastomer.

6.3.2 Tensile Testing. Tensile tests were conducted using standard test methods (ASTM, 1990a and 1990b). The exposure was made in the same pressure vessels used for the compression set measurements. Ultimate elongation measurements were taken on sample o-rings after each exposure time. Elongation to failure and tensile strength were determined by stretching each sample at constant speed until it broke. The thickness of each specimen, W, was measured at four points equally distributed around the circumference in the radial and axial directions using a dial indicator with a contact force of 0.2 N. The average of all eight measurements was used for calculation. The internal diameter of the o-ring was measured using a stepped cone with diametric intervals of 0.50 mm.

An Instron type TT-B instrument was used for the testing. Grips for testing o-rings were designed and built from low carbon steel. The grips consisted of ball-bearing spools 8.9 mm in diameter. Stresses were minimized by lubricating the contact surfaces of the spools with Super-Lube

Table 9.   Compression set after 1, 2, 4, 8, 15, 32, 48 and 74 week exposures at 5.86 MPa and 75 °C
            in the three fluorocarbon agents

Elastomer (agent)	weeks							
	1	2	4	8	15	32	48	74
S604-70 (227)	6	9	14	17	19	25	28	30
S604-70 (125)	7	8	14	31	33	35	36	39
S604-70 (218)	8	16	18	37	38	39	40	41
N674-70 (227)	12	19	28	26	31	35	38	50
N674-70 (125)	12	15	29	40	48	59	65	80
N674-70 (218)	15	18	30	35	49	59	68	79
L1120-70(227)	4	12	19	40	45	56	61	64
L1120-70(125)	15	25	41	62	68	71	74	73
L1120-70(218)	24	37	47	72	74	77	77	79
V1164-75(227)	-11	-11	-11	-4	-4	1	3	6
V1164-75(125)	-8	-6	0	6	13	14	18	20
V1164-75(218)	2	4	5	10	14	14	17	22
C1185-70(227)	12	15	22	35	52	60	66	74
C1185-70(125)	9	16	34	46	57	70	77	88
C1185-70(218)	11	20	30	35	50	65	76	85
N103-70 (227)	20	24	30	37	40	47	53	65
N103-70 (125)	21	26	41	49	60	73	80	89
N103-70 (218)	28	37	49	50	63	75	84	92
E0540-80(227)	12	14	17	15	21	24	26	43
E0540-80(125)	10	11	15	16	21	27	30	49
E0540-80(218)	9	11	17	15	24	25	30	46

o-ring lubricant. The crosshead speed was set to 50 cm/min, and a load cell with full scale load ranges of 2, 5, 10, 20, and 50 kg was used.

The ultimate elongation (U.E.) is expressed as a percentage of the original inside circumference as follows:

$$U.E. = [\frac{2D + G - C}{C}] \times 100 \, , \tag{4}$$

where D is the distance between centers of the spool grips at the time of rupture, G is the circumference of a spool, and C is the inside circumference of the specimen.

The tensile strength T.S. is the tensile stress at rupture and is calculated as F/A, where F is the breaking force and A is twice the cross-sectional area, calculated from the thickness W as $\pi W^2/2$.

The median of three measurements was used. Tables 10 and 11 show the percent change in ultimate elongation and tensile strength for all the elastomers in each agent after different exposure times at 5.86 MPa and 75 °C.

6.3.3 Extrapolating Results to Longer Times.   As discussed in Section 6.1, a major goal of this work is prediction of elastomer-agent compatibility at long times based on shorter-time measurements. We have employed two approaches here. In the first, we measure changes in mechanical properties as a function of time at fixed temperature, and fit the compression set C to a stretched exponential function $C_\infty\{1 - \exp[-(t/\tau)^\beta]\}$, where C_∞, τ, and β are adjustable parameters. If the fit is sufficiently good, the fitted functions may be used to predict results at longer times. In the second (activated process model), we seek to predict long-time behavior at lower temperatures from short-time behavior at higher temperatures by fitting the time required to achieve a given change in mechanical properties to the form $t'\exp(-\Delta H/RT)$, where t' and $\Delta H/R$ are adjustable parameters and T is absolute temperature.

6.3.3.1 Compression Set.   Figures 9-11 show log-log plots of the compression set vs. exposure time data in Table 9 for elastomers in HFC-227ea, HFC-125, and FC-218 at 75 °C. (The data for elastomer V1164-75 are not shown for agents HFC-227ea and HFC-125 because the compression set values were small or negative due to swelling.) The lines show the result of fitting the measured values of compression set for exposure times from 1 to 48 weeks to a KWW type stretched exponential function

$$C = C_\infty\{1 - \exp[-(t/\tau)^\beta]\} \tag{5}$$

where C is the compression set, t is the exposure time, and C_∞, τ and β are the fitted parameters. The values of C_∞, τ and β so obtained are given in Table 12. The data obtained at exposure times of 74 weeks have not been used in the fitting. These 74-week values may be compared with the results predicted from measurements at shorter times to assess the reliability of the fit. It can be seen from Table 9 and Fig. 9-11 that the compression set for N674-70 in agents HFC-227ea and HFC-125, and for E0540-80 in all three agents, is markedly higher after 74 weeks exposure than would be predicted from extrapolations based on the behavior at shorter times.

Table 13 shows the values of compression set obtained for elastomers in HFC-227ea, HFC-125, and FC-218 after short-term exposures at 50, 100 and 150 °C. For the activated process model, times t_{10} and t_{20} required to obtain compression sets of 10 % and 20 %, respectively, were estimated for

Table 10.   Percent change in tensile strength after 1, 2, 4, 8, 15, 32, 48 and 74 week exposures at 5.86 MPa and 75 °C in the three fluorocarbon agents

Elastomer (agent)	weeks							
	1	2	4	8	15	32	48	74
S604-70 (227)	14.4	10.9	21.5	0.3	-15.9	-6.7	-11.5	-4.6
S604-70 (125)	11.8	26.4	17.8	-8.9	-5.0	1.8	-10.3	-1.7
S604-70 (218)	12.7	14.4	12.7	-2.6	-5.8	-16.8	-0.9	-13.3
N674-70 (227)	4.6	10.7	-0.1	-65.5	-10.6	-33.4	-21.2	-42.4
N674-70 (125)	16.4	28.8	23.0	-68.6	-0.1	-25.8	-17.9	-41.8
N674-70 (218)	33.8	30.3	35.3	-66.5	-1.6	1.5	-1.6	-13.7
L1120-70(227)	17.7	-51.7	13.7	11.0	16.9	13.0	-0.1	-4.9
L1120-70(125)	28.5	7.4	40.9	-9.7	-0.1	-3.5	-0.7	-12.3
L1120-70(218)	14.1	30.2	20.8	-11.0	-4.9	1.2	-19.4	-7.8
V1164-75(227)	-6.0	-7.3	1.2	-7.7	-20.4	-44.4	-25.0	-42.6
V1164-75(125)	-38.7	-50.8	-71.9	-52.5	-75.6	-86.4	-72.5	-85.0
V1164-75(218)	12.3	28.6	10.0	-14.7	-28.6	-23.8	-15.6	-29.8
C1185-70(227)	13.8	18.9	24.2	-20.1	-23.0	-20.7	-13.4	-25.3
C1185-70(125)	18.9	20.6	15.5	-4.8	-20.7	-34.0	-20.7	-39.7
C1185-70(218)	-7.3	39.0	7.0	-12.5	-13.7	-17.0	-39.1	-44.7
N103-70 (227)	40.7	29.3	38.8	34.8	16.1	-1.2	-6.4	3.0
N103-70 (125)	33.0	51.3	46.4	27.3	15.8	-7.7	-0.3	-28.0
N103-70 (218)	55.0	59.2	40.2	16.2	10.3	3.0	1.1	-8.2
E0540-80(227)	13.0	13.0	19.9	-3.2	-4.5	-5.9	-47.7	-17.1
E0540-80(125)	13.7	19.9	9.1	-9.1	-6.8	-11.6	0.0	-7.7
E0540-80(218)	31.0	31.4	31.4	-3.2	-3.6	-14.7	-6.8	-17.1

Table 11.   Percent change in ultimate elongation after 1, 2, 4, 8, 15, 32, 48 and 74 week exposures at
5.86 MPa and 75 °C in the three fluorocarbon agents

| Elastomer (agent)	weeks				15			
	1	2	4	8		32	48	74
S604-70 (227)	3.2	-7.5	4.8	3.2	-3.8	-3.8	-10.8	3.2
S604-70 (125)	3.2	3.2	-5.9	-7.5	-0.5	6.5	-7.0	-3.8
S604-70 (218)	-2.2	-17.7	-11.3	-7.0	-3.8	-18.3	-1.6	-10.8
N674-70 (227)	-8.4	-3.0	-14.8	-12.3	-16.3	-28.3	-29.2	-44.0
N674-70 (125)	6.6	2.7	-6.3	-8.1	-18.4	-32.2	-38.3	-57.8
N674-70 (218)	1.8	-8.7	-8.7	-12.3	-20.2	-24.4	-36.1	-50.3
L1120-70(227)	8.1	-61.3	-4.4	7.5	11.9	20.0	6.3	3.8
L1120-70(125)	16.3	-20.6	15.6	-8.1	3.8	8.1	10.0	3.1
L1120-70(218)	-10.0	1.9	-24.4	-24.4	-16.3	-1.9	-38.8	-13.1
V1164-75(227)	6.1	7.8	15.1	21.8	11.2	-9.5	1.1	-8.9
V1164-75(125)	-29.6	-43.6	-59.8	-29.1	-56.4	-67.0	-50.8	-67.0
V1164-75(218)	16.8	24.6	15.1	18.4	7.8	18.4	18.4	7.8
C1185-70(227)	1.6	8.1	12.1	-17.0	-19.4	-11.7	-19.8	-24.7
C1185-70(125)	10.9	10.9	1.6	-3.6	-17.0	-22.3	-31.5	-45.7
C1185-70(218)	-8.9	10.1	-4.9	-6.5	-6.5	-8.9	-42.7	-44.9
N103-70 (227)	18.0	2.9	5.7	13.9	3.3	-13.9	-46.9	-27.3
N103-70 (125)	5.7	16.7	3.3	0.0	-13.9	-27.8	-20.4	-60.8
N103-70 (218)	13.9	2.9	-12.2	-5.7	-16.3	-30.6	-46.9	-58.0
E0540-80(227)	5.0	-1.5	6.4	-1.5	-5.0	1.5	-12.9	-14.4
E0540-80(125)	1.5	-3.0	-7.9	-7.9	-5.0	-2.0	-7.9	-11.4
E0540-80(218)	5.0	9.9	0.0	-5.0	-1.5	-5.0	-7.9	-11.4
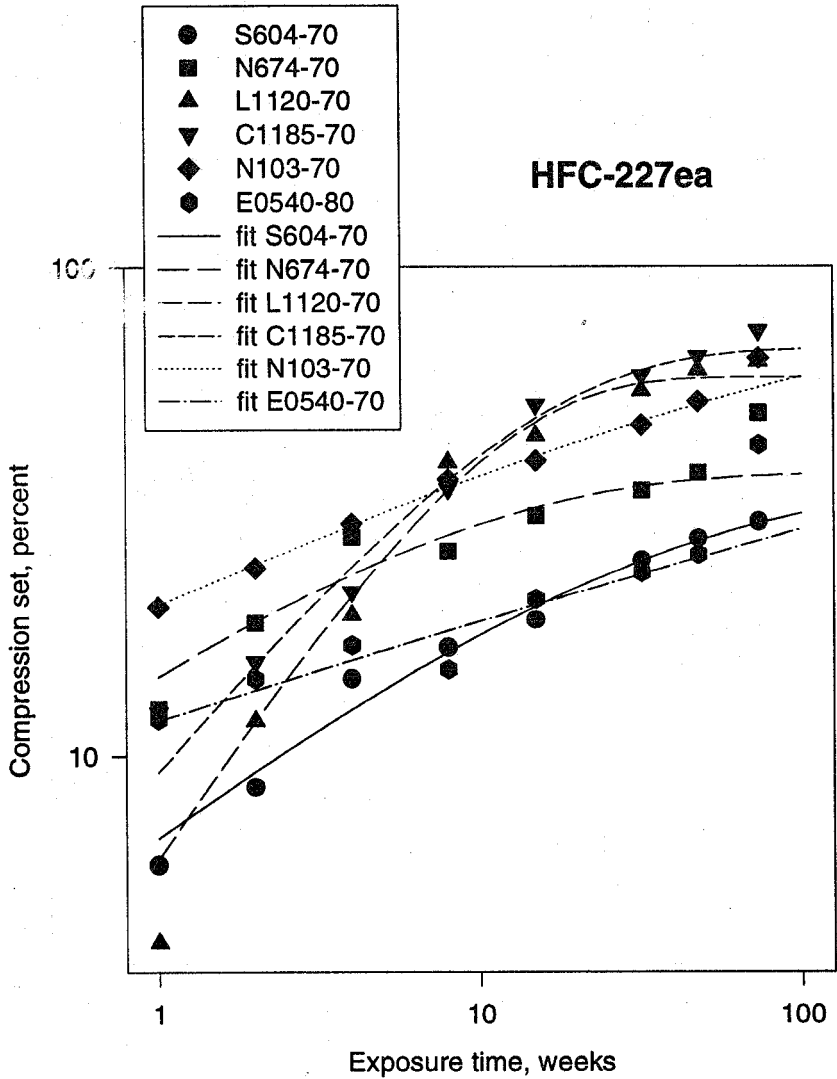
Figure 9.   Compression set for various elastomers vs. exposure time to agent HFC-227ea at
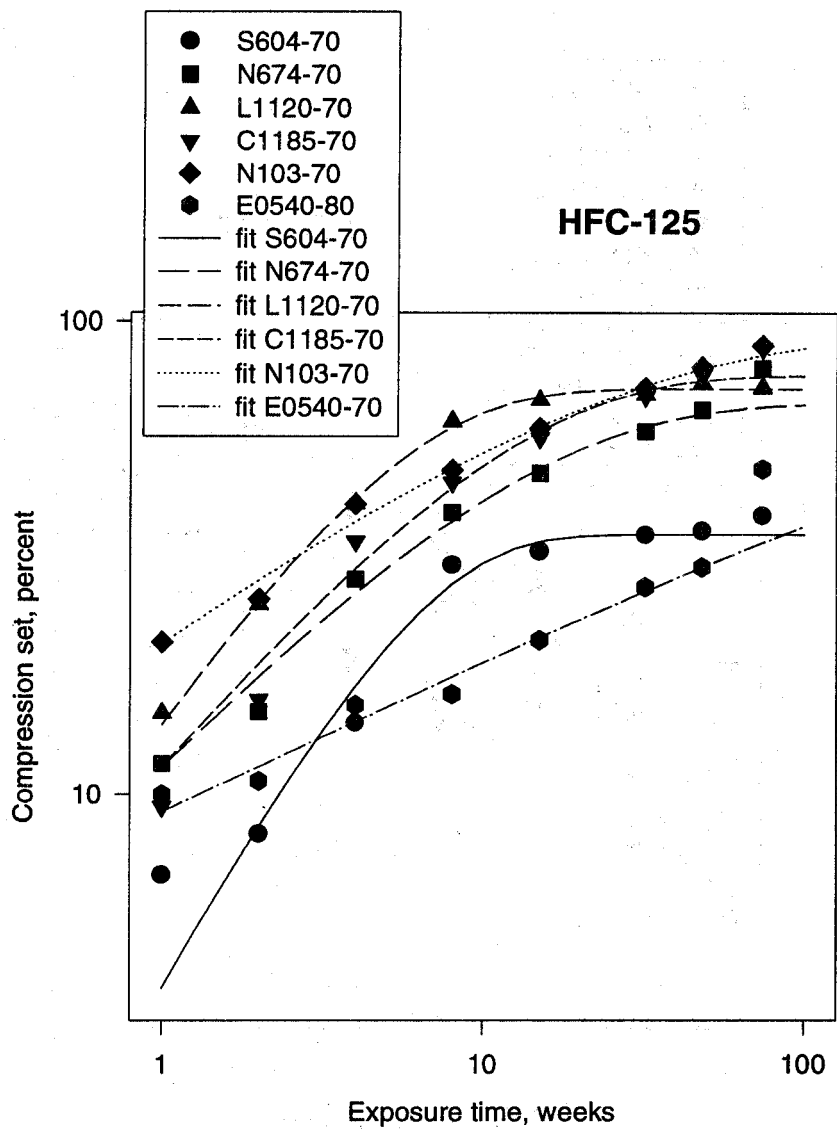   5.86 MPa and 75 °C.

Figure 10. Compression set for various elastomers vs. exposure time to agent HFC-125 at 5.86 MPa and 75 °C.
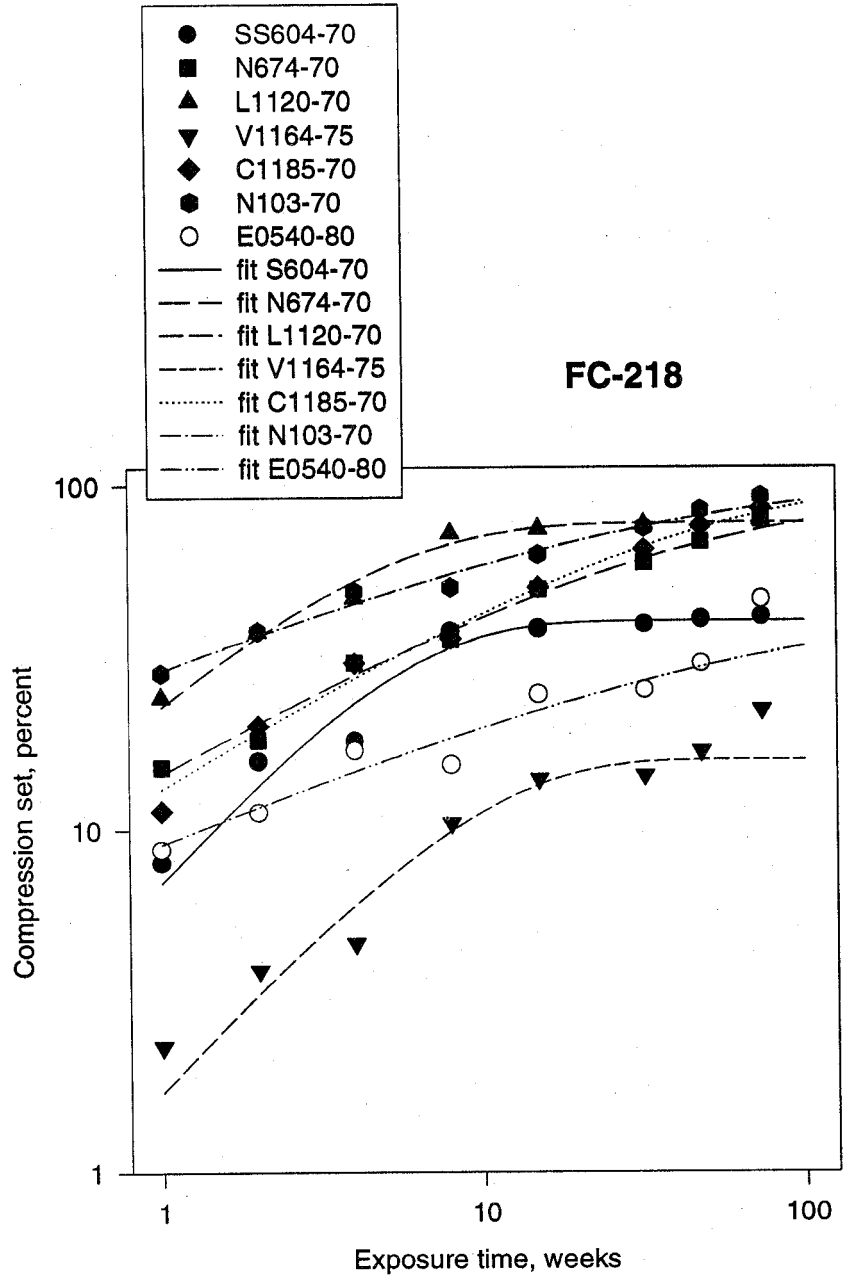
Figure 11. Compression set for various elastomers vs. exposure time to agent FC-218 at
            5.86 MPa and 75 °C.

Table 12. Parameters C_∞, τ (weeks), and β obtained by fitting compression set C vs exposure time t (weeks) to the KWW stretched exponential form of Equation (5).

agent	parameter	elastomer						
		S604-70	N674-70	L1120-70	V1164-75	C1185-70	N103-70	E540-80
227ea	C_∞	34.824	37.683	59.348	--	68.107	84.104	90.513
	τ	20.109	4.216	9.088	--	11.206	52.968	7245.738
	β	0.507	0.505	0.999	--	0.796	0.324	0.222
125	C_∞	35.548	67.433	72.261	15.828	77.22	94.216	100
	τ	5.67	10.394	4.51	12.011	9.581	14.397	953.701
	β	1.243	0.719	1.016	2.643	0.81	0.519	0.342
218	C_∞	39.854	88.16	77.387	15.803	100	100	42.19
	τ	4.6	24.164	3.483	8.102	28.241	13.98	32.139
	β	1.077	0.542	0.859	1.036	0.589	0.413	0.409
CF31	C_∞	25.866	80.446	58.51	--	79.036	89.573	40.121
	$\tau/$	11.106	9.654	5.712	--	6.04	5.85	8.594
	β	0.867	1.359	0.715	--	1.056	1.061	0.927

each elastomer-agent pair from the compression sets measured at exposure times of 1, 2, and 4 weeks, and also at 6 weeks for 150 °C exposures. The compression set vs exposure time data for each agent, elastomer, and temperature were fitted to Equation (5) by unweighted least squares. Values of t_{10} and t_{20} were calculated from the parameters so determined; they are given in Table 14. For a few of the systems, the data did not allow meaningful estimates of t_{10} and/or t_{20} to be obtained; these are shown as dashes in Table 14. In other cases, especially at 150 °C, the estimates of t_{10} and/or t_{20} are too short to be used with the activated process model. Where the data permitted, values of t_{10} and t_{20} were fitted separately by least squares to the form $\ln(t_n) = \ln(t'_n) + (\Delta H/R)_n/T$, where n is 10 or 20, T is absolute temperature in Kelvins, and $\ln(t'_n)$ and $(\Delta H/R)_n$ are the fitted parameters, shown in Table 15. From the values of $\ln(t'_n)$ and $(\Delta H/R)_n$, estimates of t_n at other temperatures may be calculated. Table 15 shows estimated values of t_n in weeks at 70 °C obtained in this way.

6.3.3.2 Tensile Testing. The percent change in ultimate elongation vs. exposure time data in Table 10 are shown in Figures 12-14 for elastomers in HFC-227ea, HFC-125, and FC-218 at 75 °C. Since many of the values obtained were negative, a linear scale has been used for the change in ultimate elongation. The scatter in the data is much too large to allow meaningful fitting to stretched exponential or other relaxation functions.

Tables 16 and 17 show the percent change in ultimate elongation and tensile strength vs. exposure time data for all the elastomer-agent pairs for short-term exposures at 50, 100 and 150 °C. As with the longer-term data at 75 °C, there is too much scatter in the data to allow meaningful fits to activation process models.

Table 13.   Compression set after short-term exposures at 5.86 MPa and 50, 100 and 150 °C.

Exposure temperature		50 °C			100 °C			150 °C			
Exposure time, weeks		1	2	4	1	2	4	1	2	4	6
Agent	Elastomer										
HFC-227ea	S604-70	4	7	9	17	23	30	25	34	48	57
	N674-70	7	10	17	34	38	47	77	84	93	97
	L1120-70	-2	1	9	39	46	52	51	56	72	83
	V1164-75	--	-13	-12	-4	-2	0	21	33	60	--
	C1185-70	9	12	15	37	42	50	66	75	81	84
	N103-70	16	19	26	47	52	57	79	87	91	94
	E0540-80	8	10	13	19	25	27	--	--	--	--
HFC-125	S604-70	3	5	9	16	21	24	33	36	50	58
	N674-70	3	6	12	29	36	56	70	84	91	96
	L1120-70	9	14	22	53	57	66	65	65	80	90
	V1164-75	--	-12	-12	4	6	15	35	46	72	90
	C1185-70	5	7	12	34	40	55	68	70	80	98
	N103-70	17	20	26	37	42	66	73	83	92	83
	E0540-80	8	11	13	18	22	26	--	--	--	--
FC-218	S604-70	3	6	10	22	24	27	41	48	50	52
	N674-70	11	14	18	39	49	60	77	88	92	95
	L1120-70	3	7	18	57	60	61	68	74	76	79
	V1164-75	--	6	8	4	7	7	25	39	56	58
	C1185-70	9	13	15	44	52	67	67	79	83	82
	N103-70	10	15	18	58	64	77	78	87	90	95
	E0540-80	7	13	15	22	24	28	--	--	--	--

Table 14. Times t_{10} and t_{20}, in weeks, to obtain compression sets of 10 % and 20 % at the exposure temperatures shown

Exposure temperature		50 °C		75 °C		100 °C		150 °C	
Agent	Elastomer	t_{10}	t_{20}	t_{10}	t_{20}	t_{10}	t_{20}	t_{10}	t_{20}
HFC-227ea	S604-70	6.9	--	2.3	6.9	0.3	1.4	0.2	0.7
	N674-70	1.9	5	0.7	2.2	0	0.1	0	0
	L1120-70	6.2	13.1	1.9	4.1	0	0.1	0	0.1
	V1164-75	0	--	--	--	--	--	0.5	1
	C1185-70	1.2	10.3	0.7	3.4	0	0.1	0	0
	N103-70	0.4	2.1	0.1	1	0	0	0	0
	E0540-80	2	13.2	0.6	11.8	0.4	1.1	--	--
HFC-125	S604-70	4.5	12.1	2.3	7.5	0.3	1.8	0.1	0.4
	N674-70	3.3	7	1	2.5	0.2	0.6	0	0
	L1120-70	1.2	3.4	0.6	1.5	0	0	0	0
	V1164-75	0	--	--	--	2.7	5.7	0.3	0.6
	C1185-70	3.1	8.6	1.1	2.2	0.1	0.3	0	0
	N103-70	0.2	1.8	0.3	1.1	0.1	0.4	0	0.1
	E0540-80	1.8	--	1.2	9.4	0.2	1.4	--	--
FC-218	S604-70	3.8	8.6	1.1	8.9	0	0.6	0.1	0.2
	N674-70	0.8	5.6	0.6	2	0	0.2	0	0
	L1120-70	2.3	4.9	0.3	0.8	0	0	0	0
	V1164-75	6.4	31.1	--	--	--	--	0.3	0.8
	C1185-70	1.3	--	0.9	2	0	0.1	0	0
	N103-70	1	--	0.1	0.5	0	0	0	0
	E0540-80	0	--	1.4	5.9	0	0.6	--	--

Table 15.   Activated process parameters and predicted values at 70 °C for compression sets C of 10 % and 20 %. Values of $(\Delta H/R)_{10}$ and $(\Delta H/R)_{20}$ are in Kelvins; times are in weeks

Agent	Elastomer	C = 10			C = 20		
		$\ln(t'_{10})$	$(\Delta H/R)_{10}$	$t_{10}(70°C)$	$\ln(t'_{20})$	$(\Delta H/R)_{20}$	$t_{20}(70°C)$
HFC-227ea	S604-70	-14.28	5171	2.2	-10.73	4310	6.2
	N674-70	-13.26	4498	0.9	-24.11	8421	1.5
	L1120-70	-14.84	5386	2.3	-19.07	6926	3
	V1164-75	--	--	--	--	--	--
	C1185-70	-8.35	2770	0.8	-32.36	11359	2.1
	N103-70	-18.05	5496	0.1	-9.34	3256	1.2
	E0540-80	-12.06	4083	0.9	-15.26	5890	6.7
HFC-125	S604-70	-16.82	5979	1.8	-12.82	5028	6.3
	N674-70	-19.81	6820	1.1	-16.28	5921	2.6
	L1120-70	-8.72	2867	0.7	-10.45	3773	1.7
	V1164-75	-18.72	7357	15.1	-17.54	7196	30.9
	C1185-70	-26.32	8963	0.8	-22.11	7883	2.4
	N103-70	-5.34	1297	0.2	-11.63	3997	1
	E0540-80	-13.88	4740	0.9	-26.13	9878	14.2
FC-218	S604-70	-15.81	5542	1.4	-15.6	5865	4.5
	N674-70	-3.64	1088	0.6	-23.98	8388	1.6
	L1120-70	-25.86	8627	0.5	-24.05	8285	1.1
	V1164-75	-10.55	4010	3.1	-12.28	5080	12.5
	C1185-70	-5.16	1743	0.9	-39.25	13915	3.7
	N103-70	-30.96	10002	0.2	--	--	--
	E0540-80	--	--	--	-32.78	12031	9.8

HFC-227ea

Legend:
- ● S604-70
- ■ N674-70
- ▲ L1120-70
- ▼ V1164-75
- ◆ C1185-70
- ⬠ N103-70
- ○ E0540-80
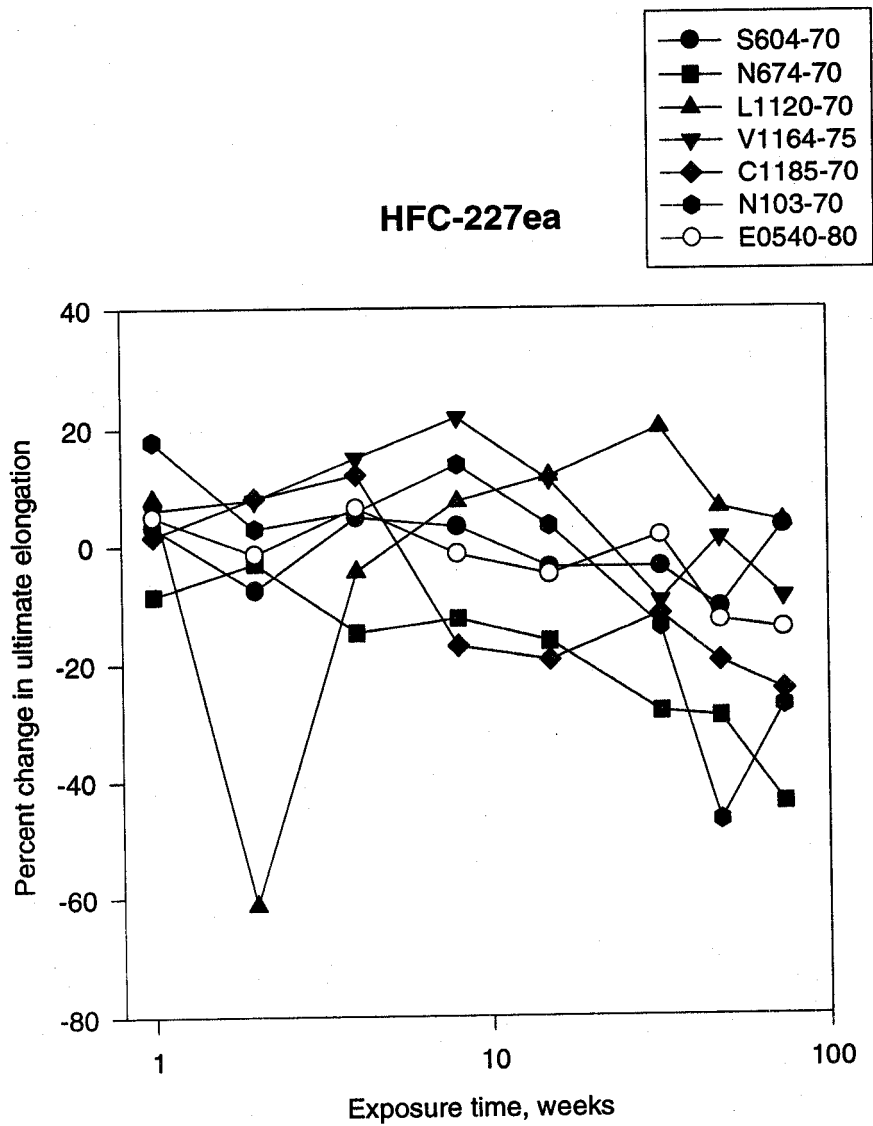
Figure 12.   Percent change in ultimate elongation for various elastomers vs. exposure time to agent HFC-227ea at 5.86 MPa and 75 °C.

HFC-125

Legend:
- S604-70
- N674-70
- L1120-70
- V1164-75
- C1185-70
- N103-70
- E0540-80

Percent change in ultimate elongation
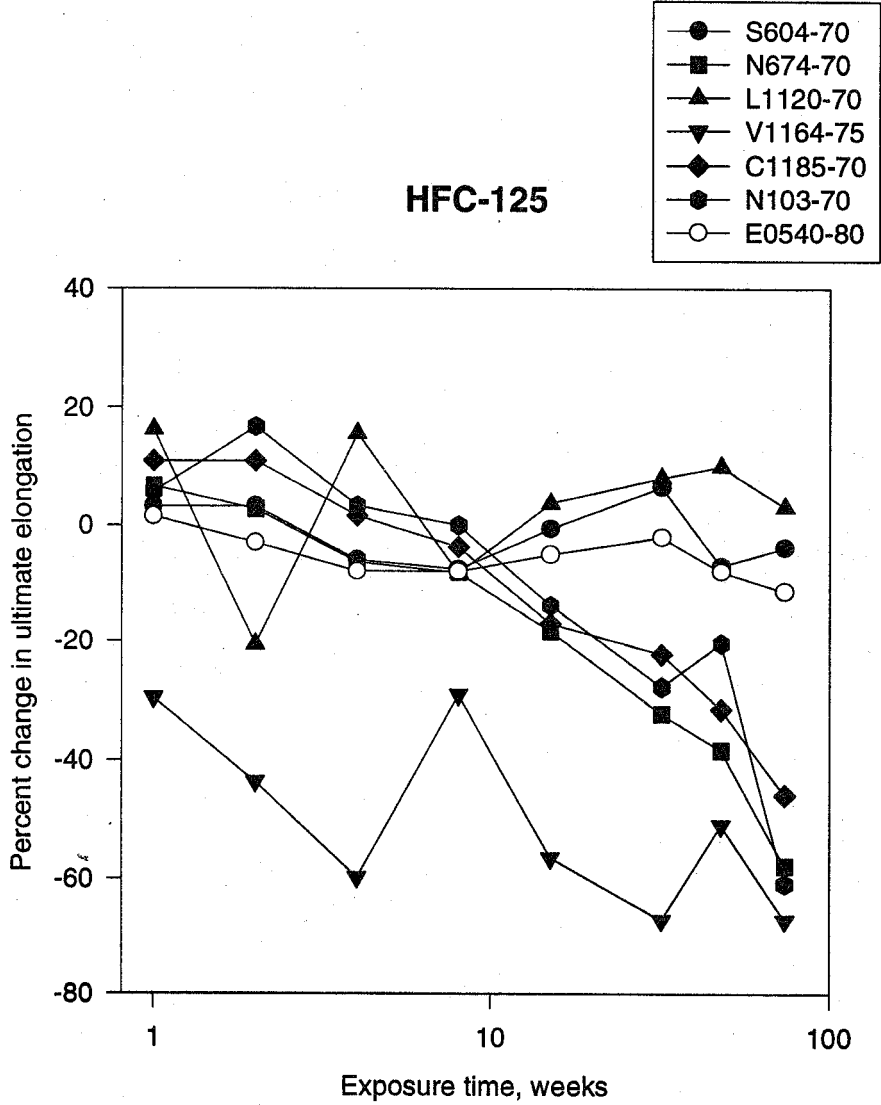
Exposure time, weeks

Figure 13.   Percent change in ultimate elongation for various elastomers vs. exposure time to agent HFC-125 at 5.86 MPa and 75 °C.
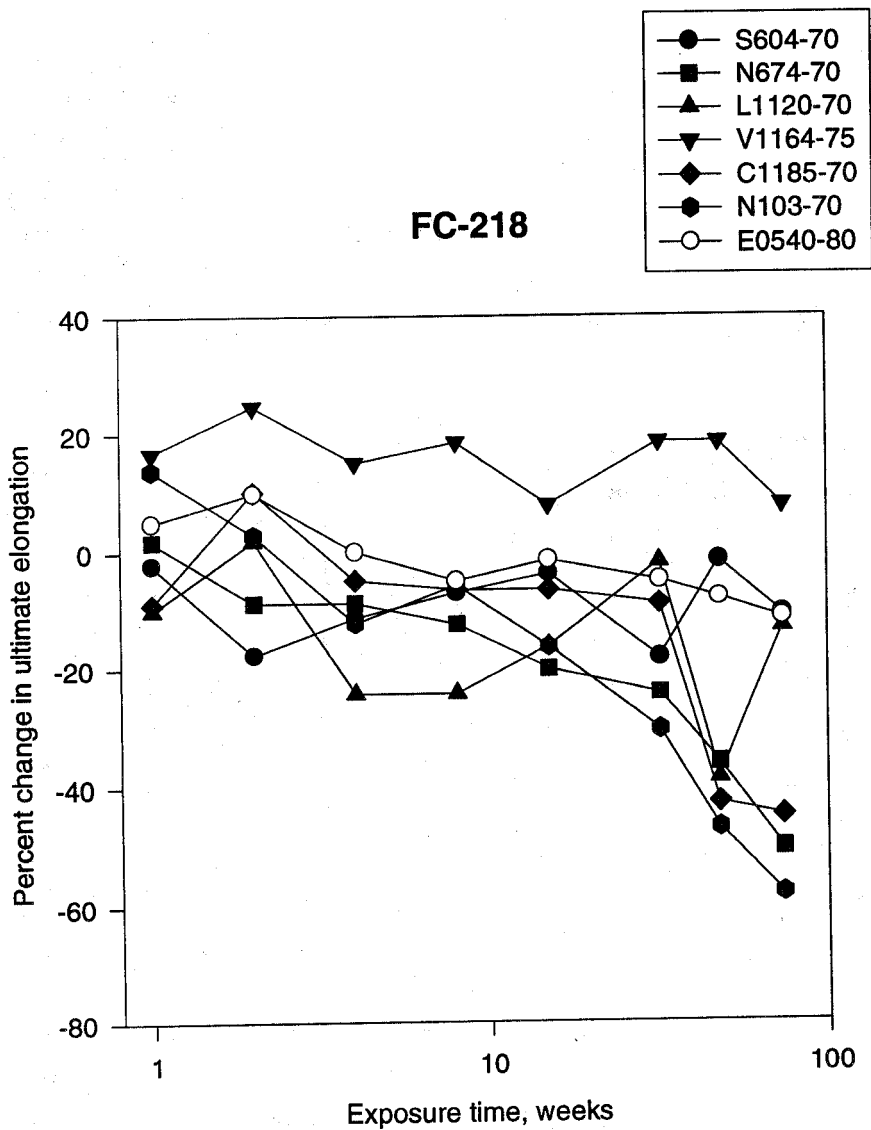
FC-218

Figure 14. Percent change in ultimate elongation for various elastomers vs. exposure time to agent FC-218 at 5.86 MPa and 75 °C.

Table 16.   Percent change in ultimate elongation after short-term exposures at 5.86 MPa and 50, 100 and 150 °C

Exposure temperature		50 °C			100 °C			150 °C			
Exposure time, weeks		1	2	4	1	2	4	1	2	4	6
Agent	Elastomer										
HFC-227ea	S604-70	-3.8	1.6	3.2	8.6	-11.3	6.5	-7.5	-10.6	1.8	6.2
	N674-70	-2.1	-7.2	-8.7	-23.2	-26.2	-40.4	-32.9	-80.7	-100	-99.8
	L1120-70	9.4	11.0	1.9	-13.1	-40.6	14.0	-17.8	-6.9	-41.4	-41.4
	V1164-75	--	6.1	7.8	0.6	13.0	-1.1	-53.9	-41.2	-62.5	-68.3
	C1185-70	4.0	-1.2	4.0	-7.7	-2.4	-27.5	-36.7	-63.9	-85.2	-95.9
	N103-70	-6.5	6.1	14.0	-6.5	-9.4	-27.8	-29.4	-79.9	-99.6	-100
	E0540-80	3.5	1.5	1.5	0.0	-5.0	1.5	--	--	--	--
HFC-125	S604-70	7.0	-3.8	-1.6	-10.8	-10.8	-8.6	-8.4	-7.1	-5.3	-10.6
	N674-70	4.8	2.7	-8.7	-20.5	-12.3	-45.2	-48.9	-74.6	-95.1	-98.7
	L1120-70	-0.6	-15.6	-0.6	41.0	33.0	14.0	-8.6	-22.4	-56.3	-75.1
	V1164-75	--	22.0	9.5	-58.1	-63.1	-58.1	-59.8	-69.6	-70.3	-87.7
	C1185-70	11.0	6.9	4.0	2.8	-8.9	-19.4	-23.8	-41.0	-63.9	-88.0
	N103-70	20.0	26.0	13.0	2.9	-18.0	-33.1	-60.8	-79.0	-94.4	-100
	E0540-80	5.0	1.5	3.5	5.0	-1.5	-3.0	--	--	--	--
FC-218	S604-70	3.2	3.2	3.2	-15.6	-3.8	8.6	1.3	-6.2	-9.3	-4.4
	N674-70	6.9	1.8	8.7	-6.3	-14.2	-32.2	-37.7	-59.1	-73.7	-81.6
	L1120-70	-8.1	-9.4	-12.5	-11.3	-19.4	-11.3	-47.9	-31.0	-43.2	-43.2
	V1164-75	--	6.1	7.8	2.2	13.0	-19.0	-50.9	-52.8	-72.2	-76.2
	C1185-70	11.0	6.9	-3.6	5.3	0.0	-11.7	-25.0	-41.4	-48.8	-58.6
	N103-70	22.0	-9.4	3.7	-4.1	-22.0	-33.5	-50.8	-72.9	-83.5	-89.0
	E0540-80	48.0	1.5	0.0	6.4	-6.4	0.0	--	--	--	--

Table 17. Percent change in tensile strength after short-term exposures at 5.86 MPa and 50, 100 and 150 °C

Exposure temperature		50 °C			100 °C			150 °C			
Exposure time, weeks		1	2	4	1	2	4	1	2	4	6
Agent	Elastomer										
HFC-227ea	S604-70	13.0	19.0	15.0	56.0	27.0	32.0	-4.6	-12.9	-15.8	-26.6
	N674-70	-1.5	-4.4	-1.5	9.2	9.2	-29.3	-8.6	-63.7	--	-92.1
	L1120-70	19.0	18.0	16.0	24.0	-20.1	13.0	131.0	-9.5	-39.9	-49.3
	V1164-75	--	-10.1	-10.4	4.5	15.0	-26.5	-51.7	-42.9	-55.0	-56.9
	C1185-70	8.7	-5.9	-1.2	26.0	6.9	-15.5	-19.6	-53.8	-74.3	-90.5
	N103-70	22.0	32.0	35.0	50.0	22.0	8.4	4.5	-51.3	-88.2	--
	E0540-80	--	--	-0.8	29.0	-4.5	4.6	--	--	--	--
HFC-125	S604-70	7.8	6.7	15.0	1.3	-3.2	1.3	-3.1	-6.7	-16.7	-32.3
	N674-70	7.5	9.0	6.1	-7.7	4.6	-36.4	-32.8	-51.5	-72.8	-87.9
	L1120-70	7.4	2.1	16.0	9.9	2.0	-2.0	-10.8	-25.9	-52.0	-76.1
	V1164-75	--	0.8	-7.7	-75.2	-80.5	-76.9	-68.5	-70.0	-54.5	-70.3
	C1185-70	5.5	3.6	0.7	0.0	-10.0	-17.5	-22.9	-32.3	-60.9	-82.6
	N103-70	31.0	39.0	29.0	20.0	12.0	1.1	-44.8	-52.7	-72.4	--
	E0540-80	--	--	-1.4	1.5	-3.2	-10.4	--	--	--	--
FC-218	S604-70	15.0	25.0	7.0	39.0	43.0	67.0	4.5	-0.9	1.5	-3.1
	N674-70	2.9	1.5	7.4	38.0	47.0	35.0	-16.0	-32.8	-42.0	-29.6
	L1120-70	13.0	21.0	3.8	27.0	26.0	42.0	-40.0	-18.1	-23.6	-28.3
	V1164-75	--	-3.1	-4.5	-7.7	6.1	-29.8	-59.1	-59.5	-67.9	-63.2
	C1185-70	7.2	-1.0	-1.2	26.0	29.0	14.0	-18.1	-33.2	-34.9	-45.0
	N103-70	15.0	-98.2	15.0	-83.9	48.0	44.0	-26.7	-45.5	-52.6	-55.0
	E0540-80	--	--	2.3	30.0	17.0	27.0	--	--	--	--

6.4 Testing of Elastomers and Lubricants in CF_3I

In this chapter the results of swelling measurements and mechanical property measurements obtained for CF_3I are reported. In the first phase of the project this agent was not investigated. It was included later in the testing programs because it was found to be very effective in suppressing non premixed flames. During the tests in this agent several anomalies were observed (the saturation vapor pressure at the test temperatures was not reproducible, oil-like residue was found in the pressure vessels after exposure, etc.). The details of the observed anomalies are described in 6.4.1.

6.4.1 Anomalous Testing Results with CF_3I. In the first lot of CF_3I both swelling and mechanical properties measurements were discontinued because of chemical purity problems. During the swelling measurements a slightly yellow solid residue developed on the Pyrex windows at 75 °C which changed from yellow to orange to a brownish red at 150 °C. Most of the elastomers were destroyed and even the stainless steel fixtures used for the compression set measurements were severely corroded after 1 week exposure at 100 °C. A high viscosity oil-like residue was found in the bottom of the pressure vessels. It was concluded CF_3I was degraded creating HI, HF and I_2. Testing with a new lot of CF_3I (Deepwater Lot #224940901) has been repeated, but our observations indicate that the saturation vapor pressure of this chemical increases after exposures at elevated temperatures. This seems to be a consequence of chemical degradation, but to a much lesser degree than in the first lot.

We found that during the exposure at a given temperature the vapor pressure of the agent was constant. Then the CF_3I was removed from the pressure vessel to a storage vessel so that the samples (o-rings) could be withdrawn for mechanical testing. When the pressure vessel was refilled with the same amount of CF_3I, the vapor pressure was significantly higher than originally, i.e., the mass of CF_3I required to attain the original pressure was reduced. The details of our observations are outlined below.

The saturation vapor pressure of the new supply of CF_3I was observed to increase after 1 week exposure at both 75 °C and 100 °C. After filling a completely dark pressure vessel with approximately 0.9 kg of unused CF_3I, the initial vapor pressure of the agent was measured as 1.66 MPa at 76.9 °C. Approximately 0.9 kg of agent was recovered and stored in a previously empty and evacuated steel tank with brass fittings for approximately 3 hours. The pressure vessel was then refilled with approximately 0.3 kg of the previously used CF_3I and the vapor pressure increased to 2.02 MPa at 76.2 °C. After another week of exposure, the vapor pressure was 2.01 MPa at 76.2 °C and then approximately 0.3 kg was recovered from the pressure vessel. For the next time interval of 2 weeks, approximately 0.3 kg was filled and recovered from the pressure vessel and the vapor pressure was 1.94 MPa at 76.2 °C. It is possible that saturation was not achieved during this exposure. A black oil was removed from the bottom of the pressure vessel and 0.8 kg of unused (i.e., fresh) CF_3I was pumped into the vessel for the next exposure. The vapor pressure was measured as 1.68 MPa at 76.0 °C and approximately 0.6 kg was recovered.

Similarly for the 100 °C exposures, the vapor pressure increased from 2.46 MPa at 99.0 °C to 2.79 MPa at 98.8 °C after recovery in the same steel tank, but the filling mass was approximately constant. Note that the quantity of filling mass must be considered carefully because any mass in excess of the amount necessary for saturation will not increase the vapor pressure. Also, this pressure vessel did have glass windows (although "UV free" PMMA sheets were used for filtering purposes) and consequently some amount of blue and ultraviolet light may have reached the agent.

These observations during exposures at 75 and 100 °C indicate possible degradation of the CF_3I, and raise a flag about the chemical stability of the material. All swelling and mechanical measurements were made with Deepwater Lot #224940901.

6.4.2 Swelling Measurements in CF_3I. The experimental method has been described in 6.2.2. All seven sets of crosslinked and uncrosslinked elastomers and lubricants were exposed to CF_3I at temperatures 35, 70, and 105 °C.

In Figure 15 the solvent uptake of the elastomers is shown as a function of the vapor pressure at 35 °C. In Figure 16 the same data are displayed according to the Flory-Huggins representation. The curves in Figure 16 show the fit of equation (2) to the experimental points. The values of the χ parameters for all the elastomers and lubricants are displayed in Table 18.

6.4.3 Durability Test Results in CF_3I. Compression set and tensile measurements were made on samples exposed to CF_3I at 5.86 MPa and 75 °C, using the methods described in 6.3. The results are given in Tables 19-21.

Figure 17 shows log-log plots of the compression set vs. exposure time data in Table 19 for five elastomers in CF_3I. (The data for elastomers N674-70 and V1164-75 are not shown because the compression set values were small or negative due to swelling.) The lines show the result of fitting the measured values of compression set for exposure times from 1 to 32 weeks to eq. 5 by unweighted nonlinear least squares. As with the other three agents, the data obtained at the longest exposure time (58 weeks) have not been used in the fitting to allow comparison of the values measured at 58 weeks with the results predicted from measurements at shorter times. The values of C_∞, τ and β so obtained are given in Table 12. It is seen from Table 19 and Fig. 17 that the compression set for S604-70 and E0540-80 in CF_3I is markedly higher after 58 weeks exposure than would be predicted from extrapolations based on the behavior at shorter times. Figure 18 shows the data of Table 20, percent change in ultimate elongation vs. exposure time for all the elastomers.

The results of tensile tests of elastomers exposed to CF_3I at 5.86 MPa and 50 and 100 °C for 1, 2, and 4 weeks are shown in Tables 22 and 23. As with the other three agents, the results of tensile tests of elastomers exposed to CF_3I exhibited too much scatter to allow meaningful fitting for the extrapolation of either time (relaxation functions) or temperature (activated process models).

6.5 Summary

In order to characterize the compatibility of elastomeric o-rings in the fire suppressant storage system, swelling and mechanical property (compression set and tensile test) measurements were conducted and data were generated on the changes in the properties of seven sets of crosslinked and uncrosslinked elastomers (silicone, fluorosilicone, neoprene, fluorocarbon, two different butadiene-acrylonitrile copolymers, ethylene-propylene-diene terpolymer) after exposure to HFC-227, HFC-125 and FC-218. In CF_3I swelling measurements were conducted for the seven sets of elastomers plus three lubricants (Krytox 240AC, Braycote 600 and Braycote 807). Exposures at 75 °C and 5.86 MPa were carried out for 74 weeks (in the case of the CF_3I for 58 weeks) to provide estimates of the long term resistance of elastomers to in-service conditions.

The following sections summarize the swelling and mechanical property estimates of elastomer performance in the fire suppressant agents. In addition, swelling performance of the lubricants is summarized. The important conclusion to be derived from these summaries and the detailed data of

Table 18.   Flory-Huggins interaction parameters χ for elastomers and lubricants in CF_3I

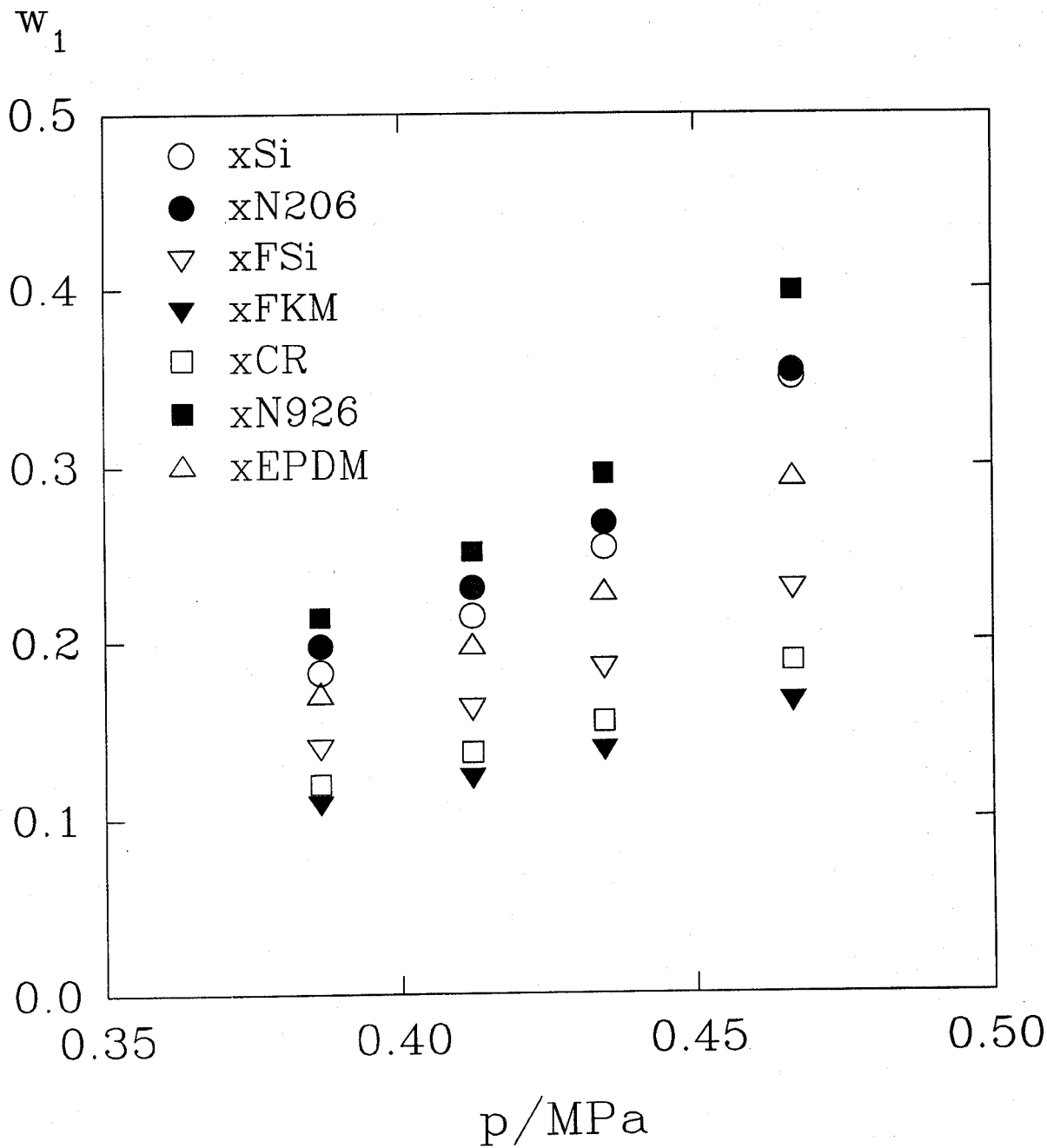| Elastomer/ Lubricant	χ (35 °C)	χ (70 °C)	compatibility
uSi	1.06	1.29	fair
xSi	1.11	1.40	fair
uN206	0.94	1.20	fair
xN206	1.00	1.25	fair
uFSi	1.20	1.41	good
xFSi	1.28	1.48	good
uFKM	1.43	1.67	good
xFKM	1.47	1.72	good
uCR	1.35	1.48	good
xCR	1.40	1.53	good
uN926	1.03	1.15	fair
xN926	0.95	1.21	fair
uEPDM	1.08	1.18	fair
xEPDM	1.13	1.25	fair
Krytox 240AC	2.11	2.12	good
Braycote 600	2.24	2.34	good
Braycote807	1.84	1.86	good

Figure 15. Weight fraction w_1 of CF_3I as a function of pressure for various crosslinked elastomers at 35 °C.
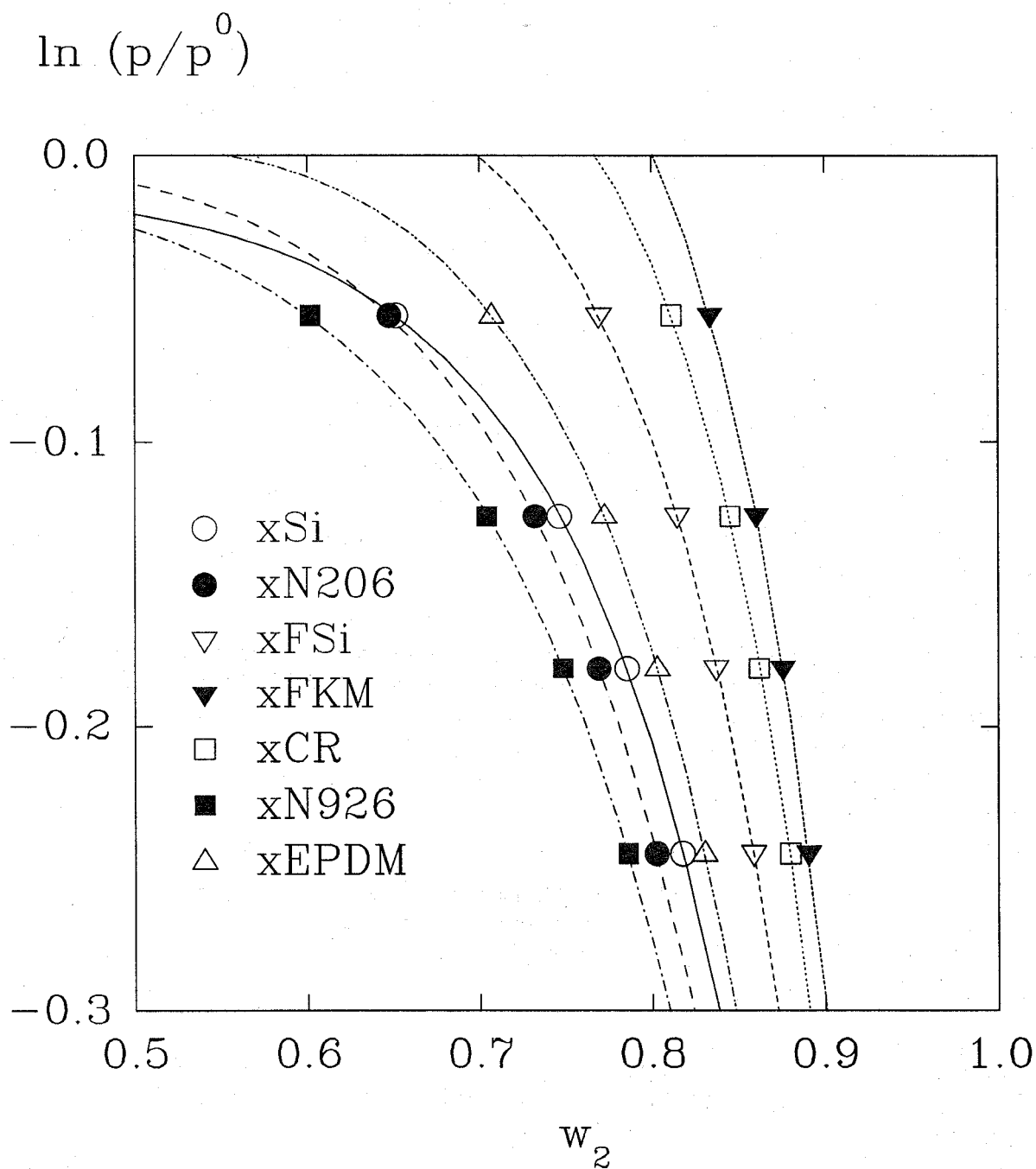
$$\ln \ (p/p^0)$$

Figure 16.   Solvent activity in various crosslinked elastomers in CF_3I as a function of polymer weight fraction w_2 at 35 °C. The curves show the least squares fits according to Equation (2).

Table 19.   Compression set (C) after 1, 2, 4, 8, 16, 32 and 58 week exposures at 5.86 MPa and
            75 °C in CF_3I

Elastomer				weeks			
	1	2	4	8	15	32	58
S604-70	2	6	8	14	18	24	33
N674-70	-3	12	24	35	70	80	81
L1120-70	13	20	36	40	48	58	65
V1164-75	-11	-5	-6	-6	-2	-1	2
C1185-70	9.1	20	43	50	76	78	81
N103-70	9	27	47	58	88	88	92
E0540-80	2	11	17	22	33	39	57

this and the prior reports (McKenna et al, 1994) is that for each of the final four agents, there exists at least one compatible elastomer and grease. It is up to the design engineer to make the appropriate selection.

6.5.1 Swelling measurements. The swelling measurements were used to make compatibility ratings based on the χ values determined for each polymer-agent system at 35 °C. Small χ values correspond to relatively high solubility or, for present purposes, bad compatibility. The results of the swelling measurements are summarized below for the four agents. An important finding is that for each agent there are several elastomers that show good compatibility, hence providing design flexibility for agent storage vessels.

HFC-227ea
     55 % butadiene-45 % acrylonitrile (N206), neoprene and ethylene-propylene-diene have good compatibility, and silicone, fluorosilicone and fluorocarbon show fair compatibility. 85 % butadiene-15 % acrylonitrile (N926) has bad compatibility. Lubricants Braycote 600, Braycote 807, and Krytox 240AC are fairly compatible.

HFC-125
     Silicon, 55 % butadiene-45 % acrylonitrile (N206), fluorosilicone, neoprene, 85 % butadiene-15 % acrylonitrile (N926) and ethylene-propylene-diene have good compatibility, and fluorocarbon has fair compatibility. Lubricants Braycote 600 and 807 have good compatibility, and Krytox 240AC is fairly compatible.

FC-218
     All the elastomers have good compatibility. Lubricants Braycote 600, Braycote 807, and Krytox 240AC have good compatibility.

Table 20.   Percent change in ultimate elongation after 1, 2, 4, 8, 16, 32 and 58 week exposures at 5.86 MPa and 75 °C in CF$_3$I

Elastomer				weeks			
	1	2	4	8	15	32	58
S604-70	0.0	10.2	17.2	6.5	31.7	-61.3	-17.2
N674-70	1.8	-2.4	-8.1	-8.1	-51.5	-56.6	-78.6
L1120-70	-20.6	-32.5	-21.9	-36.9	-21.9	3.8	-11.3
V1164-75	18.4	14.5	21.8	21.8	-10.1	11.2	-8.9
C1185-70	1.6	1.6	-27.5	-1.2	-14.2	-18.2	-32.3
N103-70	14.7	9.0	-2.4	3.3	-27.3	-67.8	-78.4
E0540-80	5.0	5.0	1.5	-5.0	1.5	12.9	11.4

CF$_3$I

Fluorosilicone, fluorocarbon and neoprene have good compatibility, and silicone 55 % butadiene-45 % acrylonitrile (N206), 85 % butadiene-15 % acrylonitrile (N926) and ethylene-propylene-diene have fair compatibility. Lubricants Krytox 240AC, Braycote 600 and Braycote 807 have good compatibility.

6.5.2 Mechanical Property Measurements. Two types of experiments were performed to produce data on residual mechanical properties of the elastomers: compression set and tensile test measurements. In order to study the effect of temperature short term (1,2 and 4 weeks) exposures to the four agents were performed at 50, 75 and 100 °C. An activation energy analysis was used to determine the temperature dependencies of the compression set data. The results of long-term exposures for 8, 16, 32, 48, and 74 weeks (58 weeks for CF$_3$I) carried out at 75 °C and 5.86 MPa have been analyzed using a KWW stretched exponential creep function. This analysis allows extrapolation to longer exposure times.

6.5.3 Compression Set Measurements. The compression set measurements showed significant differentiation between the results obtained for the elastomers in each agent after exposure at 5.86 MPa and 75 °C.

HFC-227ea

After 74 weeks exposure the compression set was small for silicone (30 %), moderate for ethylene-propylene-diene and standard nitrile (43 % and 50 %), and large for fluorosilicone, low-temperature nitrile and neoprene (64, 65 and 74 %). In the case of fluorocarbon swelling was observed.

Table 21.   Percent change in tensile strength after 1, 2, 4, 8, 16, 32 and 58 week exposures at 5.86 MPa and 75 °C in CF_3I

Elastomer	weeks						
	1	2	4	8	15	32	58
S604-70	-1.1	-0.9	5.8	-9.4	1.8	-74.2	-34.6
N674-70	4.5	3.0	3.0	-68.8	-48.5	-34.3	-69.4
L1120-70	-28.4	-40.9	-30.9	-44.1	-33.5	-6.4	-15.8
V1164-75	-20.4	-26.2	-22.8	-22.8	-50.0	-30.7	-49.2
C1185-70	-1.2	0.2	-32.0	-2.0	-30.3	-23.6	-45.5
N103-70	25.4	12.4	17.9	23.5	-14.5	-51.3	-60.0
E0540-80	1.5	-5.5	-0.8	-13.6	-21.4	-13.6	-7.4

HFC-125

After 74 weeks exposure the compression set was small for fluorocarbon (20 %), moderate for silicone and ethylene-propylene-diene (39 % and 49 %), and large for fluorosilicone, standard nitrile, neoprene and low-temperature nitrile (73, 80, 88 and 89 %).

FC-218

After 74 weeks exposure the compression set was small for fluorocarbon (22 %), moderate for silicone and ethylene-propylene-diene (41 % and 46 %), and large for fluorosilicone, standard nitrile, neoprene and low-temperature nitrile (79, 79, 85 and 92 %).

CF_3I

After 58 weeks exposure the compression set was moderate for silicone and ethylene-propylene-diene (33 % and 57 %) and large for fluorosilicone, neoprene and low-temperature nitrile (65, 81 and 92 %) In the cases of standard nitrile and fluorocarbon swelling was observed.

As a note of caution, the silicone, standard nitrile and ethylene-propylene-diene elastomers exhibited abrupt increases in compression set between 48 and 74 week exposures in some of the agents. The reader is referred to Tables 9 and 19 and Figures 9-11 and 17 for details. This indicates the difficulty of extrapolating the results to longer times than the measurements.

6.5.4 Tensile Testing. The ultimate elongation data showed very large scatter with the exposure time at all temperatures. As a result, such standard test results are not very amenable to reliable interpretation of the agent-elastomer compatibility.

Table 22.   Percent change in ultimate elongation after short-term exposures to CF_3I at 50 and 100 °C.

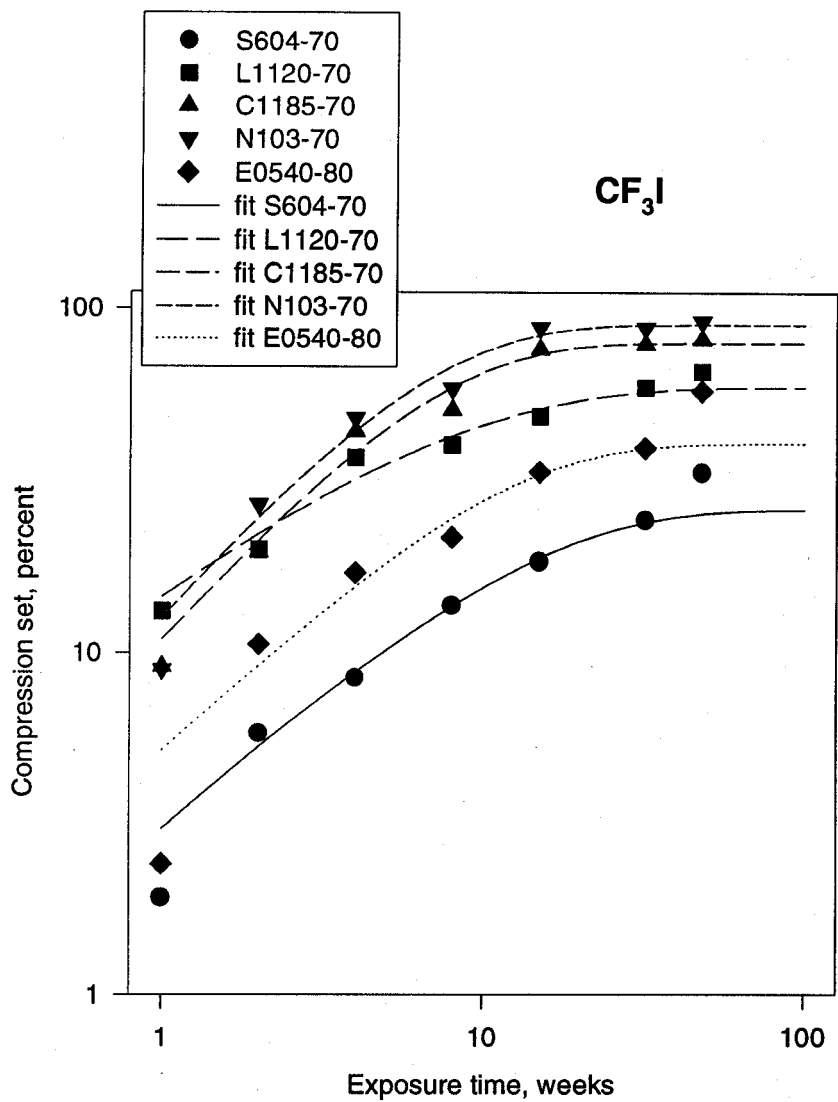| Exposure temperature	50 °C			100 °C		
Exposure time, weeks	1	2	4	1	2	4
Elastomer						
S604-70	14.0	17.0	12.0	24.0	6.5	28.0
N674-70	4.8	4.8	6.9	-10.2	-16.3	-46.1
L1120-70	12.0	16.0	1.9	12.0	12.0	12.0
V1164-70	--	13.0	17.0	11.0	7.3	7.8
C1185-70	11.0	9.3	9.3	-27.5	-11.7	-27.5
N103-70	8.2	18.0	16.0	-2.4	-8.2	-41.2
E0540-80	7.9	9.4	11.0	15.0	15.0	7.9

Figure 17.   Compression set for various elastomers vs. exposure time to agent CF_3I at 5.86 MPa and 75 °C.

Table 23.   Percent change in tensile strength after short-term exposures to CF_3I at 50 and 100 °C.

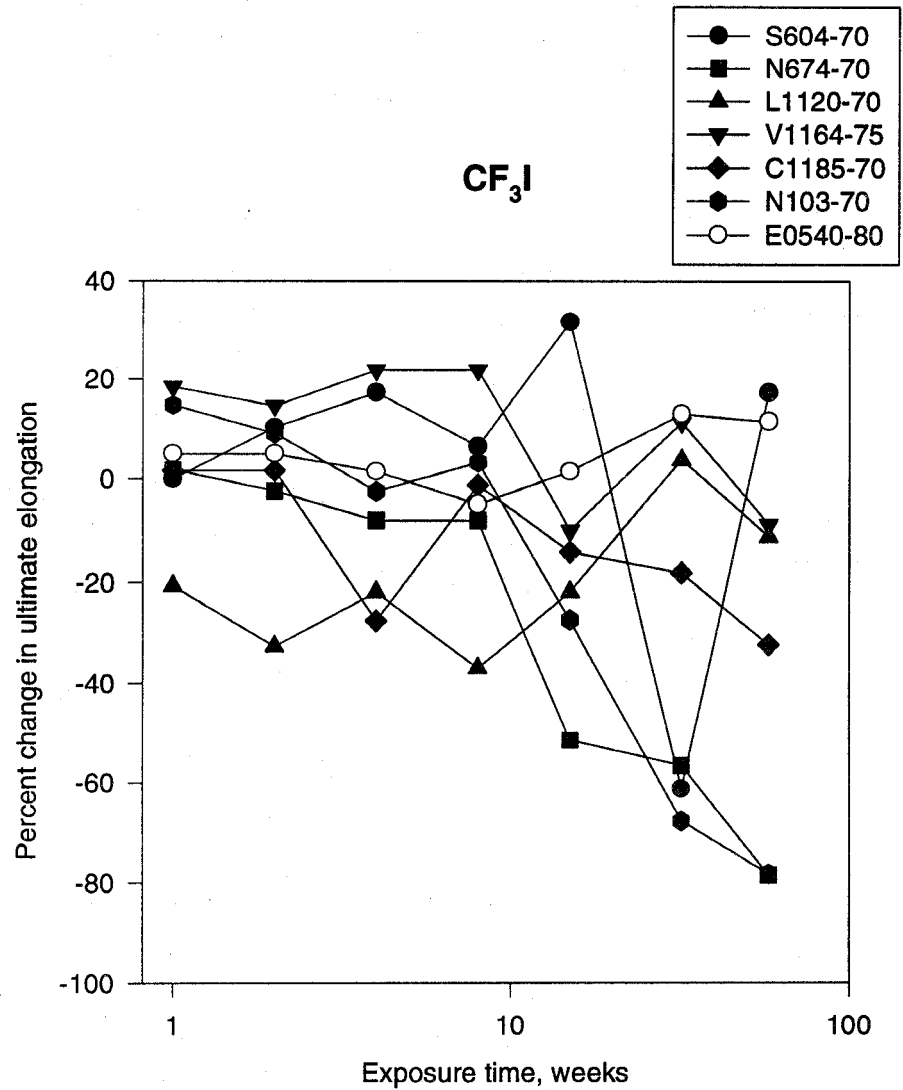| Exposure temperature	50 °C			100 °C		
Exposure time, weeks	1	2	4	1	2	4
Elastomer						
S604-70	25.0	27.0	21.0	3.9	-10.3	4.2
N674-70	6.0	3.0	7.5	4.6	-1.6	-26.6
L1120-70	15.0	13.0	3.6	-10.1	-9.5	-3.6
V1164-70	--	-9.1	-4.5	-26.2	-32.1	-29.8
C1185-70	5.8	7.2	5.2	-6.9	-10.8	-27.6
N103-70	7.5	16.0	22.0	18.0	16.0	-8.8
E0540-80	--	--	9.1	12.0	-0.8	-5.5

Figure 18. Percent change in ultimate elongation for various elastomers vs. exposure time to agent CF_3I at 5.86 MPa and 75 °C.

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